DEVELOPMENT OF HEAVY OIL HYDROCRACKING CATALYSTS

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ABSTRACT

This paper present some results obtained from the research program being pursued at the Research Institute of King Fahd University of Petroleum and Minerals aimed at the development of suitable catalysts for hydrocracking of the vacuum gas oils from Arabian Light crude to obtain higher quality distillate products. The newly developed high-performance hydrotreating catalysts are based on synthetic smectite clays and modified zeolites. Active metals have been incorporated into these novel supports to prepare several catalyst formulations for both stages of the conventional fixed-bed hydrocrackers. These novel catalysts have been characterized by sophisticated techniques and evaluated in different types of reactors (such as Pulse Microreactor, Batch Autoclave reactor, Fixed-bed Flow reactor etc.) using different feedstocks (e.g. model compounds and real VGO). Some of the formulations of developed catalysts have exhibited high performance in terms of hydrodesulfurization and cracking activities when compared to commercial catalysts under the same operating conditions. These catalysts are being further developed, comprehensively characterized, and thoroughly evaluated in order to come up with tailor-made catalyst formulations for hydrocracking of heavy petroleum fractions.

Keywords: Hydrocracking, catalyst development, heavy oil upgrading
1. INTRODUCTION

The conversion of the heavier fractions of crude oil into more valuable light products has long been a primary goal of the petroleum refining industry. Today, this goal has become even more important as the demand for heavy fuel oil and known reserves of the lighter crudes continue to decline. The market for residual fuel oil has been shrinking because of the steady increase in demand for middle distillates. Therefore, research has been aimed—especially in U.S., Canada, Japan and in Europe—to upgrade residuum. In some refineries, a large proportion of residues from distillation is not treated any further. It should be noted that about 30 percent of the Kingdom's refined product output is heavy fuel oil and only 14 percent is gasoline [Aaland, 1993]. With the commissioning of hydrocracker and continuous catalytic reformer units at Ras Tanura refinery, the overall conversion should have increased.

The overall objective of residue upgrading is to obtain additional quantities of desirable products of a higher hydrogen-carbon atomic ratio. It is worth noting that H/C ratio lies between 1.8 and 2.1 for middle distillates and lubricants, between 1.6 and 1.8 for residues, and around 1.5 for heavy crude oils. Atmospheric residues have components like resins and asphaltenes that are the most hydrogen deficient and relatively rich in carbon as well as in sulfur, nitrogen, nickel and vanadium. In general, the H/C atomic ratios of atmospheric residue, resins and asphaltenes are 1.41, 1.33 and 1.06, respectively [Beaton et.al., 1986]. The presence of these heavy molecules causes difficulties in the catalytic processing of heavy feedstocks either by hydrocracking or fluid catalytic cracking.

The Kingdom of Saudi Arabia is facing a challenge of dealing with the huge volume of petroleum residues, the demand for which is decreasing. One of the most viable options is to upgrade these residues to value-added transportation fuels by further processing. Among the residue upgrading processes available, hydrocracking is the most flexible and versatile route. Hydrocracking process is a combination of hydrogenation and cracking reactions and it is carried out at a significantly higher hydrogen pressure than hydodesulfurization. Consequently, hydrocracking catalysts contain two basic functions—hydrogenation and cracking [Satterfield, 1991] and [Ward 1993]. Hydrocracking catalysts with strong cracking function but weak hydrogenation function tend to produce lower boiling fractions (such as gasoline). On the other hand, catalysts
with weaker cracking function and stronger hydrogenation function tend to produce higher boiling products (such as middle distillates). The balance between hydrogenation function and cracking function in these catalysts can be substantially varied, so that a variety of feedstocks can be processed to produce a variety of products. Preparation and manufacture of these catalysts are highly proprietary and information available in the open literature is extremely limited. The operational severity can also be adjusted to secure an optimum group of reactions. These advantages make hydrocracking the most flexible process in petroleum refining.

This paper present some results obtained from the research program aimed at development of suitable catalysts for hydrocracking of vacuum gas oils from Arabian Light crude to obtain higher quality distillate products. The newly developed high-performance hydroprocessing catalysts are based on synthetic smectite clays and modified zeolites. Active metals have been incorporated into these novel supports to prepare several catalyst formulations for both the stages of conventional fixed-bed hydrocrackers. These novel catalysts have been characterized by sophisticated techniques and evaluated in different types of reactors (such as Pulse Microreactor, Batch Autoclave reactor, Fixed-bed Flow reactor etc.) using different feedstocks (e.g. model compounds and VGO). Some of the formulations of developed catalysts have exhibited high performance in terms of hydodesulfurization and cracking activities when compared to commercial catalysts under the same operating conditions. These catalysts are being further developed, comprehensively characterized, and thoroughly evaluated in order to come up with tailor-made catalyst formulations for hydrocracking of heavy petroleum fractions.

2. RESEARCH STRATEGIES

The research strategy has been to focus all the tasks towards the development of specific catalysts that are tailored to upgrade the vacuum gas oil (VGO) fraction of Arabian light crude oil into gasoline and diesel fuels by hydrocracking. The design and mode of operation of the existing hydrocrackers in Saudi Arabia were closely studied. The hydrocracking process in Saudi Arabian refineries is generally carried out in fixed-bed, two-stage reactors with or without interstage product separation and having inter-stage cooling. To be commercially useful, the hydrocracking catalysts being developed in this project must meet the required specifications of Saudi Aramco. In general, the hydrocrackers in Saudi Aramco are applied to produce mainly diesel from VGO. In the first-stage of hydrocracking, the target is to reduce the sulfur- and nitrogen-containing components to very low levels, while simultaneously converting 20-30% of the feedstock by hydrocracking. In the second-stage, further conversion of VGO up to 70-75% takes
place. Therefore, the catalyst used in the first-stage hydrocracking must possess excellent hydrodesulfurization and hydrodenitrogenation activities in addition to a moderate cracking activity. Hydrocracking catalysts containing NiMo or NiW as active metals, and alumina as the support, are currently being used for the first-stage. The second-stage hydrocracking catalyst, on the other hand, must possess significant cracking activity as well as be tolerant to any organic nitrogen that may remain unconverted in the first stage. Hence, zeolitic catalysts are currently being used for the second-stage hydrocracking.

Based on these specific requirements, suitable commercial catalysts were selected as reference products. Due to the major differences in the first- and second-stage hydrocracking process requirements, different reference catalysts were selected for each stage. These reference catalysts provide a baseline for comparison of properties and performance of the in-house developed catalysts. Two different routes of catalyst development are being pursued in this project: clay-based catalysts and zeolite-based catalysts. Due to the nature of these catalysts, the clay-based catalysts are more suitable for first-stage hydrocracking. They possess better hydrodesulfurization and hydrodenitrogenation activities as well as a significant cracking activity. They are also more tolerant of metals in the VGO because of their pore structure. The zeolite-based catalysts, on the other hand, are more suitable for the second-stage hydrocracking, as they possess excellent cracking activity. Hence the research strategy has been to further enhance the properties and performance of both clay-based and zeolite-based in-house developed catalysts in order to meet the specific requirements of the Saudi Arabian refineries.

In order to achieve the specific objectives, the project work has been divided into different tasks. These are research planning, clay-based catalyst development, zeolite-based catalyst development, catalyst characterization, catalyst evaluation by a pulse microreactor and a batch autoclave reactor, catalyst evaluation by fixed-bed flow and bench-scale reactor systems, feed and product analysis, and modeling of the hydrocracking process.

3. TASKS AND OBJECTIVES

The overall objective of the project is to develop a catalyst suitable for hydrocracking atmospheric residue from Arabian crude oils. The specific objectives of the project are as follows:

1. Develop analytical procedures to characterize the products (naphtha and distillate) and atmospheric residual fractions.
2. Establish catalyst preparation, pretreatment, and performance testing facilities.

3. Demonstrate the performance of hydrocracking catalysts in a micro-flow reaction system and conduct optimization studies on the catalysts identified, taking into consideration factors such as activity and selectivity.

4. Characterize the fresh and spent catalysts, feedstock, and products of the experiments.

5. Develop an appropriate catalyst for hydrocracking of the atmospheric residue from Arabian Light crude based on the above results.

Intensive and concentrated efforts were made to achieve the objectives of the project within the schedule. Essential characterization is conducted on all in-house developed catalysts. Comprehensive characterization of developed catalysts was limited to the most essential ones, if the performance is far below the target. The strategy was to perform precise and focused research and develop tailor-made hydrocracking catalysts as close as possible to the requirements of the Saudi Arabian refining industry. The specific points that were given utmost attention were as follows:

1. Enhancing markedly hydrogen transfer toward the catalyst surface to maintain the more active and more reduced catalyst surface during the reaction.

2. Regulating the pore structures to conduct fast mass transfer and prepare better support for anchoring the catalyst components. To realize this principle, bi-modal pore structures, such as micro-meso, micro-macro, or meso-macro, were designed. Achieving a three-dimensional pore structure. This is preferred to realize a better diffusion of reactants and a better durability against coke formation.

3. Maintaining the best contact in the gas-liquid-solid three-phase reaction condition of hydrocracking in both the batch autoclave and fixed-bed flow reactors. Minimizing the thermal cracking reactions in the catalyst evaluation studies and making the selective catalytic reactions predominant, which will make it possible to obtain high-quality products.

4. Analyzing feedstocks and selected products qualitatively and quantitatively for their hydrocarbon types by HPLC for assessing the activity and selectivity of developed catalysts in terms of aromatics saturation, aromatics and naphthenic ring opening, hydrocracking of the components, and overall conversion. This information was also utilized for the modeling of the reaction. This analysis can also differentiate between the performance of two catalysts having a similar conversion.
4. CATALYST PREPARATION

4.1 Clay-Based Catalyst Preparation

Recently, metal oxide pillared clays (which are expected to be a successor of zeolite) have raised great interest as a porous solid acid in catalyst development. Several studies on the properties or activities of these metal oxide pillared clays have been reported [Zubkov et.al., 1994] and [Hayashi et. al., 1997]. Since acid property is one of the important functions in a hydrocracking catalyst, there is a possibility that metal oxide pillared clay, because of its acidiy, might be used as one of the components of hydrocracking catalysts.

The catalyst support using the clay (saponite, porous saponite, hectorite, stevensite, and montmorillonite) was prepared by means of the ion exchange method as follows: 29.0 g Co (NO₃)₂·6H₂O or 29.1 g Ni(NO₃)₂·6H₂O were dissolved in 500 ml of distilled water. This solution was aged at 80 °C for 2 h. After aging, 10 g of clay were added to the solution and stirred at 80°C for 1.5 h, after which the solution was filtered. The clay was used as received or after the calcination. The residue was washed with water and ethanol, dried at 120 °C overnight and calcined at 400 °C overnight. Modified Co/clay catalysts were prepared while changing the temperature of Co aqueous solution aging or the temperature of cobalt ion exchange. (Co-Mo)/clay catalysts were prepared by impregnating the Mo (15 % as an oxide form) by an incipient wetness method with (NH₄)₆Mo₇O₂₄·4H₂O. Then it was dried at 120 °C overnight and calcined at 400 °C overnight. Al/porous saponite was prepared by the ion exchange method mentioned in 4.1.1 with 24.2 g AlCl₃·6H₂O. Mo/porous saponite (Mo:15% as an oxide form) was prepared by the impregnation (incipient wetness) method with (NH₄)₆Mo₇O₂₄·4H₂O.

4.2 Zeolite-Based Catalyst Preparation

Zeolite-based hydrocracking catalysts were prepared using the commercial Y-zeolite CT-417, supplied by CATAL, U.K., and alumina CP-100 from Alcoa. The Y-zeolite was received in hydrogen form (HY-zeolite). This zeolite was modified by steam treatment at two different temperatures of 700 to 810 °C. The steamed zeolite was used for preparing the hydrocracking catalysts. The effect of steaming was measured by the variation in the size of the unit cell determined by XRD analysis. The steam-modified zeolites were also characterized by SEM, TPD, and surface area and pore volume measurements.

NiMo catalysts were prepared by using the mixture of this steam modified Y-zeolite with commercial γ-alumina CP-100 in ratios of 50% and 30% Y-zeolite and the rest was
γ-alumina. Before mixing, the alumina and zeolite were dried in an oven at 200 °C for 2 hours to remove excess physisorbed water.

On the mixtures of zeolite and alumina, nickel and molybdenum were impregnated sequentially. The amounts of nickel and molybdenum were calculated such that the final catalyst would have 4.25 wt. %NiO and 15.0 wt. % MoO₃. For this purpose, a calculated amount of ammonium heptamolybdate (Fluka) was dissolved in distilled water. To enhance the solubility, the solution was warmed to 50°C. To this solution of molybdate a pre-calculated amount of zeolite and alumina mixture was added slowly with constant stirring. The excessive amount of water was removed by slowly heating with constant stirring over a hot plate. The partially dried mixture was placed in an oven for further drying at 50 °C over night. This sample was calcined in air at 500 °C for two hours in a programmable furnace (Isotemp Muffle Furnace 650 Series, Fisher Scientific).

On this calcined sample, which had molybdenum loaded on it, nickel was impregnated using nickel nitrate hexahydrate (Fluka). For this purpose a pre-calculated amount of nickel nitrate was dissolved in an amount of distilled water that was enough to wet the sample. This sample was again dried and calcined. The final catalyst was subjected to characterization and catalytic evaluations.

NiW catalysts were also prepared by the same procedure as mentioned above. In these catalysts, ammonium tungstate was used instead of ammonium heptamolybdate along with nickel nitrate. Ammonium tungstate was prepared in the laboratory by reacting tungstic acid (Reidel de Haen) with ammonium hydroxide (J.T. Baker 29.5% as NH₃). Ammonium tungstate was precipitated from the solution by adding excess ethyl alcohol, filtered and washed with ethyl alcohol. The final product was dried at room temperature and then at 100 °C over-night.

5. CATALYST CHARACTERIZATION

The prepared catalysts were characterized for their texture, microstructure, bulk density, chemical composition, thermal properties, crystallographic characteristics, and surface properties. Sophisticated techniques such as X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and Temperature Programmed Desorption (TPD), Temperature Programmed Reduction (TPR), Temperature Programmed Sulfiding (TPS), Electron Spin Resonance (ESR), Micro Proton Induced X-ray Emission (Micro-PIXE) Spectroscopy, Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM) were used. XPS and micro-PIXE data indicate that the active metals
are homogeneously distributed throughout the catalyst. Several new catalyst characterization techniques such as TPR-S, TPR-ESR, TPS-ESR, and TPR-S/ESR were developed. These techniques provided valuable data and insight in the structure and nature of the catalysts. Some results of the catalyst characterization studies are published elsewhere [Ahmad et al., 1999], [Hayashi et. al., 1999], [Iwamatsu et. al., 1999], [Iwamatsu et.al., 1998] and [Hayashi et. al., 1998].

The zeolite-based hydrocracking catalysts were also characterized for BET surface area and pore volume measurements. The results are given in Table 1. The highest surface and pore volume among the synthesized catalyst was found for Zeo-3. High surface area for commercial catalyst indicates high amount of zeolite present in the catalyst. Zeo-1 has also comparable surface area and pore volume. The reason for low surface area and pore volume for the catalyst Zeo-5 could be attributed to the pore blocking by tungsten.

6. FEEDSTOCK AND PRODUCT ANALYSIS

Samples of vacuum gas oils as feedstock for hydrocracking were acquired from Saudi Aramco. The hydrocracking reactions were carried out using commercial, homemade and novel catalyst systems under variable operating conditions of temperature and pressure both in batch and flow reaction systems. The feedstocks and products from these tests were characterized for their hydrocarbon types, boiling point distribution, elemental analysis and other physical properties. In addition to routine analytical methods, highly sophisticated techniques High Performance Gas Chromatography (HPLC), Fourier Transform Infra Red (FTIR) spectroscopy, Nuclear Magnetic Resonance (NMR) spectroscopy, Proton Magnetic Resonance Thermal Analysis (PMRTA), and Electron Spin Resonance were used to characterize the two oils’ fractions [Hayashi, 1998].

7. CATALYST EVALUATION

Small-scale testing of heterogeneous catalysts plays an important role during the development of a catalyst, especially at the early stages. Several types of small-scale catalyst test reactors, such as the differential reactor and the micro-reactor or isothermal integral reactor, are available. The choice of a particular reactor depends on the detailed objectives of the study to be undertaken. The cost and time required to achieve the objective should also be considered. Basic kinetic experiments are carried out using differential reactors, while integral reactors allow a high degree of conversion, which is suitable for realistic evaluations on a larger scale. To obtain detailed information on all aspects of a process, more than one type of reactor is needed.
The prepared catalysts were evaluated using batch autoclave and flow reactor systems. In order to obtain improved data for catalyst comparison, the operation technique of the batch autoclave reactor system was modified by installing a stainless steel mesh on the conventional impellor as well as by reducing the reaction time [Ali et. al., 1999].

A flow reactor system was used to evaluate the performance of the selected catalysts. Operating conditions were established for commercial catalysts so as to simulate as closely as possible the existing conditions at the hydrocracker at a refinery. The performance of commercial catalyst was studied at different space velocities to eliminate the external mass transfer effects. The commercial reference catalysts were evaluated to generate reference data for comparison with developed catalysts.

Some of the results for clay-based catalysts, obtained from evaluation tests using batch autoclave reactor, are presented in Table 2. The results indicate that the in-house developed clay-based catalysts possess equivalent HDS and cracking activities compared to those of the commercial reference catalyst. For example, the HDS activity of both Ref 1-A and Clay-5 catalysts were found to be 62 %. Similarly, cracking activity of all clay catalysts compares or even exceeds that of Ref 1-A. However, except for Clay-2 catalyst, saturates content in the product is lower, which shows the need for improvement in hydrogenation activity.

Table 3 presents the results for zeolite-based catalysts, obtained from evaluation tests using batch autoclave reactor. The results indicate that all the in-house developed zeolite-based catalysts possess comparable or somewhat better cracking activity as compared to that of the commercial reference catalyst (Ref 2-A). However, saturates content in the product is lower, which indicates the need for further improvement in hydrogenation activity.

Figure 1 presents the VGO conversion data from the flow reactor. The data indicate that the in-house developed zeolite catalyst (Zeo-1) possesses almost the same cracking activity as the commercial reference catalyst (Ref 2-A) for conversion to gasoline (b.p. <185°C) as well as to middle distillates (b.p. <375°C) at different conditions.

8. CONCLUDING REMARKS

Novel catalysts have been developed from the concept stage to the proven products for conversion of heavy oil into transportation fuels. For these valuable products to be commercially applicable further optimization of the preparation techniques of the
developed catalysts and comprehensive evaluation is essential. Intensive testing of the catalysts prepared in relatively larger scale in terms of activity, selectivity, and stability will pave the way for possible application of these catalysts in commercial hydrocracking units in Saudi Arabia or Japan. The next stage of the project will utilize the products of the first stage and carry it towards commercialization.

9. ACKNOWLEDGEMENT

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REFERENCES


Table 1.
Physical properties of synthesized zeolite-based catalysts

<table>
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<tr>
<th>S. No</th>
<th>Catalyst</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore radius (Å)</th>
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<tr>
<td>1</td>
<td>Ref 2-A</td>
<td>450</td>
<td>0.38</td>
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<tr>
<td>2</td>
<td>Zeo-1</td>
<td>300</td>
<td>0.56</td>
<td>37.8</td>
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<td>3</td>
<td>Zeo-2</td>
<td>279</td>
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<td>4</td>
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<td>302</td>
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<td>5</td>
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<td>6</td>
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<td>7</td>
<td>Zeo-6</td>
<td>287</td>
<td>0.50</td>
<td>34.5</td>
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</table>
Table 2
Catalyst Evaluation Results of Clay-Based Catalysts

Reaction Conditions:
Reactor: Batch Autoclave
Feedstock: Vacuum Gas Oil
Hydrogen Pressure: 2000 psig
Temperature: 400°C
Duration: 1 hr
Catalyst amount: 3 wt.%

<table>
<thead>
<tr>
<th>CATALYST</th>
<th>HDS Activity (%)</th>
<th>Crack Cracking Activity (%)</th>
<th>H/C Molar Ratio</th>
<th>Saturates Content (wt.%)</th>
<th>Polars Content (wt.%)</th>
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Table 3
Catalyst Evaluation Results of Zeolite-Based Catalysts

Reaction Conditions:
Reactor: Batch Autoclave
Feedstock: Vacuum Gas Oil
Hydrogen Pressure: 2000 psig
Temperature: 400°C
Duration: 1 hr
Catalyst amount: 3 wt.%

<table>
<thead>
<tr>
<th>CATALYST</th>
<th>Cracking Activity (%)</th>
<th>H/C Molar Ratio</th>
<th>Saturates Content (wt.%)</th>
<th>Polars Content (wt.%)</th>
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Figure 1  Flow reactor catalyst evaluation results for the zeolite-based catalyst Zeo-1 and the reference catalyst Ref 2-A.