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# How a 70-year-old catalytic refinery process is still ever dependent on innovation

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**Abstract**

Hydroprocessing as a catalytic refinery process is over 70 years old. Currently strong economic, environmental and social drivers are pushing the oil industry to produce more and higher quality fuels. Hydroprocessing is the turnkey technology of choice for refineries to meet these commercial demands and, consequently, catalyst vendors are being asked to design and develop more active and more selective catalysts. As a result, continuous innovation has been taking place and tremendous progress has been made in understanding the preparation and activity responses of these catalysts. Today, the refinery industry asks for ''tailored, fit for purpose'' hydroprocessing catalysts to meet their commercial goals. To meet such goals requires a deeper understanding of the complexities associated with commercial catalysts. This is a clear challenge for both academia and industry to gain the required knowledge to design and develop new and improved catalysts.



*Keywords:* Hydroprocessing; Hydrotreating; Metal sulfide; Fuels

## 1. Introduction

Hydrotreating or hydroprocessing is an established process in the refinery industry, having been first practiced before the World War II, and the technology has progressively evolved during the past 70 years [1,2]. As with any major industrial technology, the original process and its catalysts have developed according to the needs of the time. As result, today a wide diversity of process conditions, configurations and catalysts exists, although remarkably, the components of the original catalysts have hardly changed. The Co, Ni, Mo and W transition metal sulfides are still the industry favorites, given that their hydrodesulfurization, hydrodenitrogenation and hydrogenation activities, as well as their availability and cost price, have kept them in pole position. Other major catalyst ingredients such as alumina, silica–alumina and zeolites have also been exploited for a number of decades now.

A spectator outside the field of hydroprocessing may wonder what innovation is still necessary for such a ''mature'' technology. To answer such a question one must understand the drivers that keep pushing the technology and its catalysts ever forward. In this paper, we will discuss those drivers and describe how they create a need for more active, more stable and more selective catalysts. The challenge for the industry is to deliver to the market the desired innovation in the most cost effective manner. To be able to do so the technical challenges to be solved need clear definition and academia can play an important and fundamental role to study and to clarify the chemical phenomena involved with hydroprocessing catalysis. It is up to the catalyst industry to develop the new knowledge to workable solutions that are successful in the marketplace. Of course, true innovation starts where the parties understand each other's challenges and work together to develop the chemistry and technology.

## 2. Drivers

### *2.1. Refinery throughput and upgrading of low value stocks*

There are many drivers that continue to push the industry towards developing new and better hydroprocessing catalysts: the world's ever growing energy hunger, changing crude oils, new and better automotive engines, the concerns for environment and, of course, the competitive interplay between catalyst vendors. These are all important and will be discussed in more

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detail below. Two very important parameters that are sometimes overlooked by researchers are the roles of capital investment and refinery profitability. The refinery industry was faced with a situation of overcapacity in the 1980s and early 1990s. Consequently, consolidation took place within the refining industry and less profitable refineries were closed, merged or upgraded. With a steadily increasing demand for transportation fuels, capacity has progressively become limited, since very few new refineries have been built during the last 25 years, although recently there has been an upsurge concerning planning for such new refineries worldwide. Meanwhile, the industry is trying to cope with the increased demand through unit capacity creep where the existing refineries are debottlenecked wherever possible to increase the throughput. This situation creates a very strong driver for catalyst vendors to come up with more active catalysts that allow refiners to increase their throughput even further in the revamped units. The financial pay out time for loading a new and better catalyst into a hydroprocessing unit, perhaps including a minor revamp, is far less daunting than investing in a new unit. Of course, it is inevitable that such capital investments are made, to protect the longer term competitive position of a refinery. For the short term a more active catalyst, enabling higher refinery throughput, is often an economically very attractive and sound approach.

The value of crudes and intermediate products derived from them are dependent on their quality. When it comes to crudes, the refinery industry often uses the price differential between light and heavy feeds as an ‘‘economic fitness’’ parameter. Refineries that have the capital infrastructure to upgrade heavy, dirty feeds to valuable products are better positioned to build a strong competitive position and catalyst performance plays a key role in the ability to upgrade heavier feeds. This usually manifests itself in the presence of certain unit hardware, e.g. hydrocracking units, cokers or downstream hydrotreater units. Once the capital investment is made it is then up to the catalyst to maximize the economic output of the unit, i.e. maximize the conversion to valuable end products. For example, a hydrocracking catalyst that is more middle distillate selective is of value in a European or Asian refinery. Furthermore, a hydrotreating catalyst that enables a refiner to upgrade a higher percentage of low value feedstock as, e.g. light cycle oil or visbreaker oil, to a high value fuel such as diesel is preferred over a catalyst that does not.

Hence, the wish to avoid capital investment and the desire to improve refinery profitability are both strong drivers for the development of more active and more selective hydroprocessing catalysts. These incentives are quite often related to other drivers as be discussed below. However, the local economics of the refinery always determine the need and success of new and step-out catalysts.

### *2.2. Increasing energy demand and changing product slates*

The global demand for energy and in particular transportation fuels keeps growing [3]. Oil consumption rose from about 70 million barrels per day in 1995 (one barrel is 158.98 l) to over 80 in 2005 and is projected to grow to over 90 million barrel per day in 2020 [4]. While a significant part of the growth is located in North America, the largest growth is observed in the Asia Pacific region. The future growth of energy demand in the Asia Pacific area has recently seen a series of announcements for new grass root refineries, mainly to be located in the Middle East and Asia Pacific. Current predictions indicate that only 60% of all new announced projects will actually materialize. Nevertheless, this still provides an extra capacity of about 12–13 million barrels per day in 2015 relative to current capacity [4]. It is clear that new refineries imply new hydroprocessing units and further growth of the total market for hydroprocessing catalysts.

Globally, the product slate of refineries is changing as result of a relative growth of demand for diesel, at the expense of gasoline, due to the increasing popularity of the diesel car. Even in a gasoline based country as the US, the sales of diesel passenger cars and light duty vehicles is increasing, leading to a significant shift in refinery product demand. This is just one reason for the recent industry need for hydrocracking unit catalysts that are more middle distillate selective while refiners need to debottleneck these units even further. Quite often hydrocracker units are limited in their pretreat section, where the organic nitrogen must be brought down to enable the downstream hydrocracking catalyst to function appropriately. Debottlenecking of the hydrocracker thus creates a need for more active pretreat catalysts.

### *2.3. Heavier and more sour crudes, new crude sources*

Though slow, there is a continuous trend within the refining industry that the crudes are getting more heavy (higher density) and more sour (i.e. containing high amounts of sulfur). A prediction by Hart is that in the upcoming 15 years an extra 0.15 wt.% of sulfur will occur in crude to then give an average level of 1.28 wt.% [4]. Also, the shift in crude diversity and source will continue. For example, more Russian and Caspian crude import is expected in Western Europe, and these crudes are heavier and contain higher amounts of contaminant metals as e.g. As, compared to the traditional North Sea and Middle East crudes. The effects from heavier crude supply are thus twofold. Since the demand for light products is increasing at expense of heavier fuels (e.g. heavy fuel oil), more crude conversion will be needed to upgrade the heavy crudes to give the desired product mix. Secondly, the higher level of contaminant metals in the feed will necessitate more effective guard bed catalysts and systems.

A very exciting and emerging field is the production of syncrudes in Canada and Venezuela. The Canadian syncrudes are produced from tar sands by a process of extraction and bitumen upgrading [5]. The upgrading of these tars sands, via bitumen, to Synthetic Crude Oil is most challenging with respect to hydrotreating since the bitumen contains two to four times as much sulfur, nitrogen and aromatics compounds as regular crudes. The levels of As and Si contaminants present can be quite high, which creates its own problems in such processing schemes. Operational conditions for hydroprocessing of these types of crude are much more severe compared to processing of conventional crude fractions. Consequently, the experience with