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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 conventional hydrotreating catalysts operating under these sorts of conditions is limited and it can be assumed that opportunities will open up with the development of tailored catalysts for this area.

2.4. Innovation in engines and the automotive industry

The automotive industry is under heavy pressure from regional, state and government legislation to develop cars that have high fuel efficiency (low CO_2 emissions) and emit a minimum of pollutants such as SO_x, NO_x and particulate matter. Intensive research takes place and continuous progress is made with the development of better and cleaner engines and catalyst exhaust systems. Without addressing all the subtleties of the developments, these developments directly result in a need for fuels that are even cleaner than we have today. Recently, major truck manufacturers showed that the reduction of total aromatic content of diesel to <5 wt.% results in a large reduction in emissions (30 wt.% particulates, up to 28 wt.% CO, 4–10 wt.% NO_x) without any loss of engine performance, compared to normal 10 ppm S diesel (EN590) containing 25 wt.% aromatics. The truck manufacturers concluded that the low S–low aromatics diesel with high cetane number is potentially the ‘‘fuel of the future’’. Two other examples are given in the Worldwide Fuel Charter of 2006 [6]. A direct correlation is reported between diesel cetane number and the NO_x and hydrocarbon emissions, where an increase in cetane number from 50 to 58 results in a 26% decrease of emissions. Similarly, reducing the sulfur content of diesel fuel has an impact on the formation of particulate matter. Part of the SO_2 emitted is converted to sulfate, which in turn acts as seed for formation of a particulate matter. Similar relationships have been found between quality of the fuel and emission levels for gasoline.

This need for high quality fuels will continue to grow in the upcoming years and refiners will have to invest more in upgrading facilities. Among such refinery capital expenditure, hydroprocessing is a favorite choice since it combines the removal of contaminants as sulfur and nitrogen with the concomitant upgrading of the fuel properties.

2.5. Environmental concerns: low sulfur, low aromatics and biofuels

The importance of environmental concern as a key driver for development of better hydroprocessing catalysts has already been addressed in the former section. Legislation mandating less emission of SO_x, NO_x, VOC and particulate matter have led to a continuous tightening of the specifications for transportation fuels. These changes in specifications are not limited to diesel and gasoline, but also extend to heating oils and marine fuels. Furthermore, while Europe, Japan and North America are leading in adapting to new tighter specifications, the rest of the world is following. It will not be long before ultra low sulfur diesel and gasoline will be standard transportation fuels throughout the world.

With diesel and gasoline, the tight specifications on sulfur content in particular have led to a wave of innovation in hydroprocessing catalysts and processes. For gasoline upgrading, SCANFINING^{TM} and Prime-G^{TM} have together taken the market share for selective desulfurization. With diesel, major leaps have been made in developing more active HDS catalysts, for example Albemarle’s STARS^{TM} and Nebula® catalysts and developments in these fields are still progressing. A good example of the impact of changing specifications on refinery operation is the upgrading of Light Cycle Oil (LCO). Produced in the FCC unit, LCO is viewed as a refractory, difficult feed to hydroprocess, typically containing 1–3 wt.% S and 60–90 wt.% total aromatics. The worldwide FCC capacity is about 716 million tonnes/year, thus yielding ca. 143 million tonnes LCO/year. Up to 35–40 vol.% LCO is typically blended into heating oil and off-road fuel, which contain 0.2 and 1.5–2 wt.% S, respectively, and subsequent form a major source of SO_2 emissions when using such fuels. These traditional outlets for LCO will become less and less available as a result of tighter fuel specifications. Consequently, refiners must find a way to upgrade LCO in existing facilities, with use of suitable catalysts, or invest in new upgrading units. The treatment of LCO is difficult and results in a high hydrogen consumption to produce acceptable hydroprocessed products. With the currently often limited H_2 supply in the refineries, it is crucial to find ways to convert these feedstocks to more valuable fuels with acceptable H_2 consumption, necessitating ‘‘hydrogen management’’ for clean fuels. This is another example where a newly developed catalyst can provide increased added value by avoiding or at least postponing capital investment.

Recently, the refining industry focus and attention for conversion of biofeedstocks into usable transportation fuels has exploded. The use of catalytic processes in the production of first generation biofuels (ethanol, FAME) is however limited, although catalysts are essential for the development of second-generation biofuels. Second-generation biofuels are usually characterized by the high quality of the resulting fuels or the use of the whole, and not just a part, of the biofeedstock (e.g. Bio to Liquids). The number of patent applications on the use of hydroprocessing as an integral process for upgrading biofeedstocks, and vegetable oils in particular, is growing [7–9]. An important challenge in upgrading these and other biofeedstocks is the removal of the organic oxygen that is contained in the feeds [10]. Metal sulfide catalysts have proven earlier to be effective for hydrodeoxygenation (HDO) of coal derived liquids [11] and have been studied for their application in upgrading of biomass derived feedstocks.

3. Challenges

Having reviewed the major drivers that are fueling the demand for new and better hydroprocessing catalysts, what are the challenges that are faced in catalyst development?

3.1. More activity for HDS, HDN and aromatics removal

There is a continuous pressure of refiners to develop hydroprocessing catalysts that are more active for hydrodesuphurisation (HDS), hydrodenitrogenation (HDN) and aromatics saturation. Recent Albemarle advances such as STARS^{TM} and Nebula$^{®}$ catalysts have made considerable and successful market penetration. Still, there is a need to improve and, in particular, to tailor catalysts for specific application segments. For example, a catalyst that is extremely active for HDS of middle distillates will not automatically deliver a similar good performance on vacuum gas oil. Consequently, due to the other type of sulfur and nitrogen species present in vacuum gas oil, the optimization of the active phase is different and has to be adjusted accordingly. Similarly, the textural properties of the support, e.g. surface area and mean pore diameter, need to be optimized to cope with a particular class of feedstocks [12]. Apart from activity itself, also the intrinsic balance between HDS (∼hydrogenolysis) and HDN (∼hydrogenation) sometimes needs optimization depending on feedstock, operating conditions and available hydrogen. Hydrogen availability at the refinery is often limited and hydrogen consumption is fast becoming a key contributing factor within the variable costs of operating the unit.

Overall a refinery's H_2 consumption increases as HPC severity increases (deep HDS, more aromatics saturation) [13]. Traditionally a refinery's H_2 supply mainly came from the reforming process (cyclization of paraffins and aromatization of cycloparaffins produce $1H_2$ and $3H_2$ per molecule, respectively) and to a lesser extent from alternative sources such as partial oxidation (POX) or steam methane reforming (SMR). The H_2 source and "supply chain" within a refinery infrastructure is now changing fast with clean fuels legislation and constitutes major considerations and capital investment for refineries. The future reduction in the gasoline aromatic content will lead to less H_2 generation from reforming. Refinery H_2 needs may be in balance with the reformer capacity in the current refinery but the H_2 supply will be insufficient in the future. The future challenge is to reconfigure processes for clean fuels production at the lowest H_2 cost while meeting product quality specifications. Solutions must be sought to minimize H_2 consumption, maximize H_2 production and eliminate H_2 losses to fuel (through solution losses and loss to fuel gas). The refiner has to maximize the H_2 production in the reformer or H_2 plant and maximize the selectivity of catalytic hydroprocessing reactions in order to consume H_2 selectively and avoid over-treating the products if there is no added value. In that respect, aromatic saturation is not always desired unless the resulting volume swell (through density reduction) pays out or there is need based on further downstream processing or fuel specifications.

The challenge is to develop hydrotreating catalysts that deliver more volume activity combined with the desired selectivity and "directed" hydrogen consumption.

3.2. Selectivity of conversion catalysts

As the demand for middle distillates is growing so is the need for middle distillate selective hydrocracking catalysts. Hydrocracking catalysts contain acidic components as zeolites and amorphous silica–aluminas in order to crack the feedstock into the desired product range. A hydrocracker's product slate demands vary according to geographical location of the refinery and commercial markets associated with that refinery. Many hydrocrackers are operated to produce middle distillates in Europe and Asia whilst maximising throughput. This requires catalysts that have a high selectivity towards middle distillates at the highest possible conversion. Incremental steps of an extra 1 or 2% conversion can already contribute significantly to the hydrocracker's economics. The challenge for catalyst vendors is to tune the acidic properties, and then the interplay between the acidic function and the active metal sulfide phase in order to optimise the cracking and hydrogenation functions.

3.3. Demet and guard bed catalysts

With ever increasing levels of contaminants in the crudes (Ni, V, Fe, Si, As), new and improved guard catalysts are necessary. In particular the upgrading of bitumen and other oil sands derived feedstocks offers a challenge with respect to their very high levels of metal contaminants. In applications where a feed with contaminants is being processed, guard catalysts are applied to protect the downstream high activity catalysts. These guard catalysts are often applied as stacked systems containing more than one type of guard or "demet" catalyst. Typically, guard bed catalysts are applied to trap moderate amounts of Fe, Ni or Si for lighter distillate hydroprocessing applications such as processing of vacuum gas oils or coker gas oil. So-called demet catalysts are invariably used in case of resid type of applications where metal contaminants are often present in relatively high concentrations. These catalysts are designed to trap large amounts of metals (e.g. Ni, V) that are present in resid feedstocks. As these metals are present in the oil feedstocks, in the form of bulky molecules like asphaltenes, a lot of know-how on demet catalysts is in the design of the pore architecture. Next to absolute activity, the lifetime of these catalysts and their maximum metals uptake capacity is of utmost importance and often more critical than their initial activity.

The trend towards heavier feeds and new crude sources such as tar sands asks for guard and demet catalysts with higher metals uptake capacity and efficiency in removal of metal contaminants. The resid catalysts that are applied in ebullated bed reactors form a special case. Compared to fixed bed reactors, the catalyst particles are mixed with the feed and operated in a slurry mode as an expanded catalyst bed, where these catalysts incorporate all necessary functions such as HDS, HDN and demet activity. It is a true challenge to design and develop catalyst grades for this type of application that are effective as well as have a decent lifetime.

3.4. Staging of catalysts

As already mentioned, a catalyst loading scheme of an industrial hydrotreating reactor seldom consists of a single catalyst. A division can be made between the guard bed, the demet catalyst and the actual HDS/HDN catalysts. In addition to that, a combination of HDS/HDN catalysts is more effective than a single catalysts in a number of cases. A good example is the application of staged beds for ULSD operation where a combination of NiMoP and CoMo catalysts results in a better overall performance than a single, full loading of either of the single catalysts [14]. It is a proprietary know-how of catalyst vendors to forecast the performance of these staged bed systems and it is interesting to note that innovation may not come through new catalyst compositions but also through a new stacked bed system comprising different catalysts.

4. Science and catalyst development

The above paragraphs described the drivers and challenges in the industry with respect to catalyst development. We have demonstrated that, after a history of over 70 years of hydroprocessing, there is still a compelling need to improve over the current catalyst technology. These improvements can and are often regarded as incremental, not representing a real step-out change for either technology or science. In comparison to other emerging or fast moving fields such as computer science or biocatalysis, the relative progress made in the development of new catalysts and catalyst systems is indeed smaller, reflecting the maturity of the field. On the other hand, there is a still a wealth of knowledge yet to be learned. For example, the exploitation of new crude sources, such as biofeedstocks and tar sands, open up new opportunities for step out technology outside the current field of expertise.

4.1. Higher performance catalysts—how can science continue to contribute?

Research on metal sulfide catalysts and hydroprocessing is one of the most elaborately studied fields of catalysis. There is a wealth of multidisciplinary knowledge relating to the nature of the active phase, reaction mechanisms, catalyst design and reaction kinetics. How can science contribute further to help the industry in reaching their goals for catalysts development? What is the benefit for science and the academic catalysis community to develop their knowledge in this field? We believe that there are a number of research topics that remain unresolved and need to be addressed, not only for the merits of hydroprocessing but also for the propagation of catalysis science.

4.1.1. Selectivity and catalyst activity in a regime of inhibition

It is very well known that hydrotreating catalysts contain different types of active sites that are active for hydrogenolysis and hydrogenation, respectively. It is also known that the selectivity or ratio between the two type of active sites can be tuned by, e.g. choice of promoter metal (Co or Ni), preparation conditions and support properties. It is understood that various organosulfur, organonitrogen and aromatic compounds compete for adsorption onto the actives sites of the catalysts in its working state. It is also understood that this adsorption then results in inhibition of the actives sites and that some sites are more susceptible to this inhibition than others. However, how to minimize the effects of this inhibition phenomenon is poorly understood. For example in the area of ultra low sulfur diesel (ULSD), the focus of many authors and researchers has been on the removal of the so-called sterically hindered sulfur species as 4,6-dimethyl-dibenzothiophene [15]. Studies have shown that these compounds can be desulfurized via two different pathways: pre-hydrogenation and direct hydrogenolysis. Intuitively it was therefore concluded that NiMo catalysts are intrinsically more suited for deep desulfurization since they are more active for hydrogenation than CoMo catalysts. Also, in commercial operation it has been observed that operating pressure and feed refractory sulfur content determine the choice between CoMo or NiMo catalyst for this application [16]. However, an even more important parameter is actually the presence of organic nitrogen species in the feed. Various studies have been published that demonstrate that efficient removal of the organic nitrogen species from the feed boosts the HDS activity and the removal of refractory sulfur [17–23]. So, the challenge in developing more active HDS catalyst is not just limited to understanding how to boost HDS activity for refractory sulfur, but in understanding how to minimize the effect of inhibitory nitrogen species.

This brings into focus the broader theme of catalyst selectivity. A chemical feedstock often consists of a single or limited number of components in quite a few areas of industrial catalysis. Catalyst selectivity is then often referred to as the ability of the catalyst to convert the specific reactants to the desired products. In hydrotreating of oil fractions, the feedstock is a mixture of thousands of components. Selectivity is interpreted as the broad activity response towards HDS, HDN, aromatics saturation and cracking. The challenge is to understand and to control the selectivity in this environment of competing and inhibiting species. That is truly an area of research that is worthy of further investigation [24–27].

4.1.2. Activation of hydrogen

The focus of many researchers in hydrotreating has been on the activation and reaction pathways of the sulfur and nitrogen species. Less attention has been paid to the activation of hydrogen; this is rather remarkable from the perspective of the industrial operations. In most cases, the mid distillate hydroprocessing unit is operated in a trickle flow mode of operation, resulting in the surface of the catalyst being covered with oil. The necessary hydrogen for reaction is dissolved in the oil and transported to the active sites on the catalyst. Even in the ‘state-of-the-art’ trickle bed reactors, the effectiveness of the catalyst is limited by diffusion into the pores of the particles. Consequently, due to limited H_2 solubility, the inside of the catalyst may be starved for H_2 when in the presence of high amounts of aromatics. For selective hydrogenation, the elimination of diffusion limitations is paramount, so that activation takes place on the active sites and hydrogen can participate in the reaction. A number of authors reported studies on hydrogen activation [28–33]. However, most of them unfortunately relate to gas phase reactions with an abundant supply of hydrogen to the surface of the working catalyst. It is well known that the hydrogen partial pressure and flow rate have a big impact on catalyst activity and stability for commercial trickle flow reactors. Furthermore, there is an inverse relationship between hydrogen consumption and deactivation rate in commercial units where hydrogen availability is low. It would be a step forward in reaction dynamics if the relationships between H_2 transport, activation and H_2 starvation in trickle flow reactors were better understood.

4.1.3. Controlling the active phase dispersion

Clearly, the dispersion of the active metal sulfide phase has a direct relationship with the activity of the catalyst and the selectivity for HDS, HDN and dearomatization. A series of proposals modeling the structure of the active phase have been reported over the last decade [34–43]. In addition, studies to describe the relationships between preparation conditions, the structure of the oxidic precursor catalyst and the structure and catalytic performance of the active sulfided catalyst have been carried out. In industry, impregnation of pre-shaped bodies is a common process to manufacture hydroprocessing catalysts. Recently, new insights were obtained in the relation between composition of impregnation solution and the nature of the active metal species deposited on such extrudates. The use of spatially resolved Raman and UV–vis spectroscopy has enabled this type of research and deepened the understanding in this field [44,45]. This type of studies can be applied in the industry to examine their, often proprietary, combinations of carrier materials and metal precursor. In the academia, the findings of fundamental studies like the one mentioned can be transported to other areas of heterogeneous catalysis for benefit of the whole community.

Typically, preparation of catalysts is an area that benefits from progress that is made with the advancement of *in situ* spectroscopy techniques. This creates new insights and eventually leads to innovation in commercial manufacturing recipes and techniques. Combined with today's power of high throughput experimentation, substantial progress is and can be made in the industrial design and development of catalysts.

4.1.4. Deactivation and conditioning of the working catalyst

Life would be great, although somewhat boring to some respect, should carefully designed and prepared catalysts keep their initial characteristics during their entire life cycle. In practice, the structure and morphology of the active metal sulfide sites in the working catalyst are susceptible to changes, being dependent on the reaction conditions the catalyst was exposed to during its lifecycle [38]. Recently, it was demonstrated in commercial catalysts that the promoter metal Ni or Co segregates from the Mo upon sulfiding and subsequent use of the catalyst [46]. A next step could be to apply the understanding gained for designing smarter catalysts that can cope with their ageing and adapt accordingly. Self-repairing materials is an emerging area of research in material science and why should heterogeneous catalysis not profit from that as well? Self-repairing materials are characterized by their ability to repair emerging cracks or other deficits in their structure upon damaging. The mechanism of repairing is executed by a chemical or physical moiety that was installed in the material at its fabrication. A review of these materials was reported by Takeda et al. [47].

4.1.5. New materials allowing higher volume activities

Reactors in refineries are fixed in size and ''drop-in'' catalyst solutions, having more activity, are welcomed by the industry. So, whereas scientific papers are often referring to weight or molar activity, volume activity is the criterion that is applied throughout the industry. Volume activity is the rate constant for e.g. sulfur or nitrogen removal expressed per unit of volume of catalyst. There are various ways to improve volume activity. A recent commercial example is the development of a new metal sulfide catalyst, called Nebula® [48]. This catalyst is extremely active and a step-out change in comparison to other commercial catalysts. In most cases, the commercial process and the unit equipment were not designed for the heat release and H_2 consumption accompanying such high activity catalyst. The commercial use of such high activity catalysts can only be accomplished by close cooperation between the catalyst manufacturer, process licensor and the refinery.

Today, most commercial catalysts are still based on alumina as a carrier material. Alumina offers a great deal of advantages as a carrier support, e.g. thermal stability, good mechanical properties, a controllable pore structure and a tunable interaction with active metals as Mo, Ni and Co. In both the design and control of the textural properties of aluminas, progress can still be made. The purpose of the carrier is to provide a surface for dispersing of the active phase and a pore structure to allow access to the active phase. Unfortunately, a trade off exists between surface area and accessibility. Alumina, and other materials, with high surface areas often have a high percentage of their pore volume stored in micropores. In hydroprocessing, the mesopores (1–30 nm) are important to allow sufficient access for the liquid oil. For example, mesoporous materials as MCM-41 with the desired carrier properties have been reported for use in hydroprocessing catalysts [49]. Commercial introduction has so far been limited due to the high manufacturing costs of such materials and the difficulties in controlling the dispersion of the active phase. Additionally, these carrier materials often have low density and cannot meet the volume activity targets of the refinery units.

There is a need from the industry to develop new carrier materials as well as catalysts. Science could contribute here by not only focus on the materials itself, but by studying the interplay with the other components that make up the catalyst. The new era of catalysts is one of clever design and integration of the active, supporting and promoting components. The design rules are, however, still rudimentary and often based on experience, rather than on hard scientific evidence.

4.1.6. Guard bed and demet catalysts

As discussed above, current and future crudes, among others bitumen and oils sands based crudes, will contain higher levels of contaminants as Ni, V, Fe, Si and As. The design of effective guard bed catalysts and catalyst systems is a special case that differs from the design of HDS and HDN catalysts. The contaminant metals that are removed from the feed by catalytic reactions are deposited onto the catalyst [50–54]. To ensure a decent lifetime of such catalyst the clever design of the pore architecture of the catalyst bodies is necessary and several metals deposition models have already been presented [55–58]. Science could contribute in this area by providing deeper insight on the structure and nature of the contaminant metal species in the mineral oils and studies concerning the reaction mechanisms that lead to deposition on the catalysts.

4.1.7. Upgrading of biomass through hydroprocessing

Upgrading of biomass by using hydroprocessing creates new challenges for design and development of the catalysts. The main reaction taking place in hydrotreating of biomass is hydrodeoxygenation (HDO) of the oxygen containing hydrocarbons in the biomass. New insights into the mechanisms of HDO and of the behavior of traditional CoMo and NiMo catalysts were recently reported [59]. Since new feedstocks are being tried and upgraded via various process routes there is still much to learn on the reaction mechanisms of biocompounds and the catalyst performance seen.

5. Conclusions

Though hydroprocessing is over 70 years old we have demonstrated that innovation is still occurring in this area of refinery catalysis. Strong economic, environmental, legislative and social drivers are pushing the industry to produce more of the higher quality fuels. Hydroprocessing is one of the turnkey processes for helping refiners to meet their challenges. Catalyst vendors are therefore being pushed to design and develop better catalysts.

Hydroprocessing has been an area of research by the catalysis community for a very long period of time. However, there are major challenges still to be met in the fundamental study of hydroprocessing reactions and catalysts. The chemistry involved is complex and does not allow for easy solutions, either from the catalytic application itself or from the catalyst manufacturing point of view. *In situ* analysis and study techniques for use in catalyst genesis and preparation, as well as in its working state, are essential to understand the underlying principles for the design of improved catalysts. As complex as these challenges are, the solutions are just as rewarding for both industrial and academic researchers.

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