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Catalysts for Hydroprocessing of Heavy Oils and Petroleum Residues

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Abstract

With the increasing demand of petroleum-derived products due to the world population and development, upgrading of crude oil with heavier quality and petroleum residues is unavoidable. Hydroprocessing is a preferable process for heavy oil upgrading. The process is operated with the presence of a catalyst, and catalysis plays an important role in the process. An overview regarding the catalyst design such as the catalyst active metal, active phase, support properties, and catalyst structure for heavy oil hydroprocessing is provided. There also include some recent advancements related to catalytic hydroprocessing of heavy oils and residue processes. Further catalyst performance improvement will likely come from catalyst optimization and better catalyst deactivation resistance resulting from metal poisoning and coke formation.

Keywords: heavy oil, residue, hydrocracking, hydroprocessing, mesoporous, macroporous

1. Introduction

The increasing world population and economic growths cause significant increases in oil demand. With the finite conventional fossil fuel reserves, the production based on alternative renewable sources and nonconventional oils such as heavy crude oils and tar sand bitumen is expected to increase. Heavy oil, as the general term for nonconventional heavy feedstock, is considered as an alternate suitable source for transportation fuels, energy, and petrochemicals to fulfill the requirements of modern civilization [1]. This indicates that processing of heavy oils in the petroleum refining industries is growing.

In general, heavy oil is defined as any liquid petroleum with an API gravity less than 20°. API gravity is an expanded density scale used widely in petroleum industry. Heavy oil with API gravity below 10.0°API sinks under the water as it is heavier compared with water (10.0°API), and it is termed extra-heavy oil [2]. Compared with conventional light oil, heavy oils have higher viscosity, higher density, and lower API gravity. The properties of heavy oils vary according to its origin and synthetic route.

The main issue with heavy crude oil is that it produces a lower percentage of gasoline and diesel fuels and a higher percentage of residue fraction when distilled by an oil refinery. In addition, heavy crude oil has more negative impacts to the

environment than its light counterpart, and its refining requires the use of more advanced techniques. Petroleum residues are the heavy fraction remaining after distilling petroleum crudes at atmospheric pressure (atmospheric residue) or at reduced pressure of 25–100 mmHg (vacuum residue; boiling point $>525^{\circ}\text{C}$). Petroleum residue has high average molecular weight (> 1000 Da number average for vacuum residue) and higher asphaltene content [3]. Asphaltenes are insoluble in n-alkanes such as n-pentane and n-heptane but soluble in benzene or toluene [4]. In addition, residues have high heteroatom content such as sulfur (~ 5 wt%), nitrogen, and heavy metal (i.e., vanadium and nickel > 100 ppm). These heteroatoms tend to poison catalysts and cause problems during processing and, therefore, need special processing in the refinery to remove them.

Petroleum residues can be converted into lighter oil or more value-added products using bottom-of-the-barrel conversion processes or residue upgrading processes [1]. No matter which type of process is used, a substantial fraction of residue molecules can be cracked off as fragments to become liquids in the transportation fuel and vacuum gas oil boiling ranges. However, due to the high asphaltene content, overly converted residues can push the selectivity toward the thermodynamically favored but lower valued products, namely, coke and hydrocarbon gases.

Hydrogen addition and carbon rejection are the two major approaches to upgrade petroleum residues into lighter oils in petroleum industry. Carbon rejection, such as coking process, produces a lot of cokes during the heavy oil upgrading processes which have low or no market value. In the past few decades, hydrogen addition approach especially hydroprocessing has gained prominence in heavy oil or vacuum residue upgrading processes [1]. This approach upgrades heavy feeds to distillate fractions and generates less coke.

Various hydroprocessing reactor technologies such as fixed-bed, ebullated-bed, or slurry-phase reactors are used to upgrade heavy residues [5]. The principles of these reactor operations are almost the same but differing with respect to some technical minutiae and tolerance of impurities [1, 6]. Typically, hydroprocessing of heavy oils is an upgrading process carried out at temperature around $380\text{--}480^{\circ}\text{C}$ and hydrogen pressure at 80–270 bar with the presence of a catalyst [7]. H-Oil™ and LC-Fining are the processes designed to convert heavy residue to lighter fractions by hydroprocessing using an ebullated-bed reactor. Eni slurry technology (EST) and CanMet by Energy Research Laboratories, Canada, are examples that are using slurry-phase reactors.

In general, hydroprocessing involves hydrocracking and hydrotreating. The main objective in heavy feedstock upgrading is to convert heavier residue into lighter distillates in such a way to increase hydrogen-to-carbon (H/C) ratio of the product. Thus, hydrocracking reaction is the main concern. Hence, sometimes hydroprocessing of heavy oils is also called hydrocracking of heavy oils. During the process, larger molecules such as asphaltenes and resins are cracked and being converted to lighter liquid hydrocarbons such as gasoline, diesel, and gas oil. Meanwhile, various hydrotreating reactions such as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodemetalation (HDM) are also occurring during the process under the operating conditions. This leads to better product oil quality and contributes toward hydrotreating process in the later stage.

Hydroprocessing is the most versatile of the modern heavy feed conversion processes. The flexibility of the operating conditions with respect to both the feedstock and product separation has provided the most economical refinery balance relative to supply and demand [1]. Catalyst plays an important role attributed to this flexibility in hydroprocessing, in which upgrading the most problematic feeds such as vacuum residue is derived from heavy crudes, as well as the direct upgrading of the latter. During reactions, catalyst helps to reduce the activation

Reactor type	Catalyst size, mm [8, 9]	Catalyst in reactor, particle/cm ³ [9]
Fixed bed	~1.2–3.0	120
Ebullated bed	~0.8	250
Slurry system	~0.002	2.4 × 10 ⁹

Table 1.
Typical catalyst properties for residue hydrocracking.

energies leading to higher yield and selectivity for the products in favor. Various factors influence the product selectivity; these include reaction operating conditions and catalyst properties such as active sites, shape, size, chemical compositions, etc.

Reaction operating conditions associate directly with the productivity. Heavy oil hydrocracking is typically carried out at a relatively higher temperature. Since the reaction operating conditions for different technologies are different, to ensure the desirable yield and selectivity, it is important to consider the characteristics of the feed, appropriate reactor system, and catalysts for the hydrocracking of vacuum residue [1].

For different types of reactor operation, the catalyst properties especially the catalyst particle sizes deployed also vary. The typical catalyst properties used in different types of reactors are given in **Table 1**.

Generally, supported sulfide catalysts containing group VIB and VIII metals especially cobalt, molybdenum, tungsten, or nickel are used in heavy oil upgrading processes. However, impurities present such as heavy metals in the residues decrease the catalytic activities [1, 10].

Establishing an understanding of the key catalyst properties that influence catalyst performance in hydrocracking of heavy residue is important. This provides a basis to develop a better-performance catalyst for heavy oil hydrocracking.

2. Catalyst design for hydroprocessing of residues

Hydrocracking reactions require a bifunction catalyst with high cracking and hydrogenation activities. The high cracking activity is provided by an acidic support, whereas the hydrogenation activity is provided by metals on the support. The acidic catalyst support, such as acid-treated clay, alumina, or silica-alumina, is used to promote cracking and support the metals such as nickel, tungsten, platinum, and palladium that supply the hydrogenation function. These highly acidic catalysts are sensitive to the feed with high-nitrogen compound, which easily neutralizes the acid sites. Therefore, catalyst used for heavy oil hydrocracking process is different from the normal distillate hydrocracking process. Further, heavy oil that is derived from different geographical areas possess different properties. Therefore, it is important to have a specific designed catalyst that is suitable to the targeted heavy oil hydrocracking. Here, a key challenge is to design and synthesize catalysts that have high activity for hydroprocessing. Main components in catalyst design for hydroprocessing of heavy oils are discussed in the following sections.

2.1 Transition metals for hydrocracking catalyst

Cracking of C—C bonds require a high amount of energy; therefore, hydrocracking reactions occur significantly only at high temperature (~400°C and above). The main function of catalysts is to provide hydrogenation-dehydrogenation reactions that lead to higher liquid hydrocarbon yield and

suppress coke formation. Platinum-group precious metals such as platinum and palladium are the representative catalysts with excellent hydrogenation capacity, and they are also commonly used in many other reactions. However, these platinum-group precious metals showed weak resistance especially to sulfur [11]. Sulfur escapes and reacts with the catalyst during upgrading process as extra-heavy oil containing high concentration of sulfur [12]. Therefore, in order to cope with heavy residue, which is high in sulfur content and other impurities such as nitrogen, and heavy metals that can easily deactivate or poison the catalyst, platinum-group precious metals have not been used as catalysts for the upgrading of extra-heavy oil.

Mo, Ni, Co, and W are the common established transition metals used as the active ingredient in catalyst for hydrocracking of heavy residue. Sulfides of Mo and W are usually used, and Ni and Co are used in promoting species components in the petroleum industry. These metal sulfides not only promote relatively high hydrogenation but are also good in hydrotreating activities such as HDN, HDS, and HDM during heavy residue upgrading process. The abovementioned metal sulfides are favored as well in terms of their availability and the cost comparing to the noble metals such as platinum and palladium. There are also studies on using other promoters such as phosphorus (P), fluorine (F), and boron (B) on the catalysts [1].

The reactive metals are usually deposited on catalyst support by wet or incipient wetness impregnation methods. The impregnated catalysts are then calcined, reduced, and used for the hydrocracking reactions.

2.2 State of active phase

Sulfides of metals, e.g., MoS_2 and WS_2 , have been used as the active phase in hydrocracking catalyst. NiMo and CoMo sulfides were identified to exhibit superior HDS activity [13, 14].

Sulfidation of supported oxidative metal catalysts is normally carried out by thermally reacting with sulfur compound prior to hydroprocessing in order to have the best catalyst performance. For dispersed catalyst, sulfidation of the catalyst can be done either ex situ or in situ. Most oil-soluble catalyst metal precursors, which are available in the oxide, can be sulfided in situ by thermally decomposing sulfur compound in the heavy residue upon the reaction severity and transformed from inactive oxides to sulfides during the upgrading process [15]. However, the complete sulfidation of active components can be challenging [16], and incomplete sulfidation reduces the catalyst performance to a certain degree. Dispersed metal oxide catalyst can also be presulfided ex situ by using H_2S as the sulfiding agent followed by dispersion in oils [14].

Sulfidation is a complex reaction. Strong interaction between metal and support can cause poor reducibility of the metal species, which eventually makes the sulfidation of the catalyst difficult and leads to poor activity [17]. In spite of similar activities for the hydrocracking reaction, W-based catalysts have received less attention than Mo catalysts. This is due to their lower sulfidation ability, on which the catalytic activation is strongly dependent [18].

Carbide catalysts are also being tested in heavy residue upgrading [19, 20]. Studies have shown that the electron distribution of the d orbitals and consequent catalytic activity of WC are similar to those of platinum, while the resistance to sulfur is higher than platinum [21]. Density functional theory (DFT) studies have shown that WC can act as a catalyst with a strong hydrogenation capability without being poisoned by sulfur [22]. However, there are problems with carbide catalysts such as nano-sized particles of WC are difficult to obtain because of the high temperature in the carburization process, and metal contamination occurs when WC in bulk is obtained through a ball milling process [20, 23].

2.3 Properties of support material—acidity and porous structure

Catalyst support plays an important role in a catalyst. Support provides space for the active metal to stay upon as well as acid sites for cracking activity. Large surface area of support is generally favorable for catalyst as it can be interpreted directly into more active sites available on the catalyst surface which normally lead to better catalyst performance. Porous structure support exhibits large surface area. Hence, other than the chemical composition of catalyst, textural properties of support such as size, shape, surface area, and porosity have a great influence especially for heterogeneous catalyst system.

2.3.1 Acidic properties of the support

Acid sites of the catalyst promote cracking activity. Materials such as alumina, crystalline zeolite, amorphous silica-alumina, and mixture of crystalline zeolite and amorphous oxides with high acidity (Lewis and Brønsted acid sites) are used as catalyst base or support in order to promote more cracking activity during reactions. These supports usually have a structure with numerous micropores (pore diameter < 2 nm), which provide high surface area and acidic properties [24].

In terms of chemistry at the molecular level, zeolites and amorphous silica-alumina share some similarities. However, zeolites, which have the crystalline structure, offer higher activities and better controlled selectivity than the amorphous materials. Typically, using zeolite-based catalysts in hydrocracking results in greater cracking activity owing to its greater acidity. In addition, the use of zeolite-based catalyst improves thermal or hydrothermal stability and resistance to nitrogen/sulfur compounds.

However, catalyst deactivation occurs quickly when these conventional supported catalysts are used in heavy residue hydroprocessing. This is due to pore blocking caused by relatively high concentrations of heteroatoms, metal poisoners, and asphaltenes commonly found in heavy fractions. This significantly reduces the availability and accessibility of the active sites at the catalyst surface in the pores by the reactant molecules. Hence, conventional supports are not suitable for upgrading of extra-heavy oils and vacuum residues. It is also believed that the catalyst support's intrinsic acid sites (e.g., $\gamma\text{-Al}_2\text{O}_3$) participate in sediment or coke formation during hydrocracking reaction [25]. To avoid pore blocking problem, this leads to the introduction of meso (2–50 nm)/macropores and high pore volume into the catalyst support for hydrocracking catalyst.

Therefore, greater attentions are paid to the properties of catalyst especially support materials such as the size of the particles, pore volume and pore size distribution, and the shape of the particles to maximize utilization of the catalyst.

2.3.2 Support material porosity and pore size distribution

High asphaltene content in heavy oils leads to a higher tendency to form coke during processing compared to conventional light crude oils. This is due to the accumulation of the coke precursors on both external and internal configurations of the catalyst. In addition, rapid deposition of metallic poisons narrows down the catalyst pore size, restricting the accessibility by reactant species and products. These may cause complete pore blockage. As a result, the catalyst activities and performance reduce markedly. Hence, typical good catalyst design for heavy oils upgrading processing must offer (1) accessibility to large asphaltene agglomerates in order to increase their diffusion and transformation and (2) catalytic active sites or support adsorption sites that are less favorable to sediment or coke formation [3].

Also, it is clear that the pore structure of the catalyst has a close relationship with the conversion, selectivity, and stability properties of the catalysts during hydrocracking reaction [26].

In order to overcome the difficulty of asphaltene diffusion through small pores, the development of the porous shaped support or catalyst structure with macropores (>100 nm) is rationalized. However, too many macropores (ca. above 30% of total pore volume) should not be created, since shaped particles could turn fragile [3]. Mesoporous alumina is a rigid porous material with a mutually interconnected or isolated network structure which has not only the characteristics of a crystalline phase of alumina but also the characteristics of a porous material [27]. Catalysts having pores between 7 and 20 nm diameter showed higher activities than those catalysts having pores between 3 and 7 nm which was reported for hydrocracking of Athabasca oil sand bitumen [28]. In order to retain the mechanical strength, stability, and accessibility to large asphaltene agglomerates of the catalyst during heavy residue hydrocracking reaction, the multimodal porous structures or hierarchical pore system is developed in hydrocracking catalyst. Hierarchical pore system in catalyst not only integrates different functionalities in the catalyst but also allows the realization of a multiple step reaction in one single catalyst in a cascade way without any separation processes.

Hydrotreating effect especially HDS of atmospheric residue is a well-established residuum upgrading process which requires catalysts designed to remove and accumulate metals and to desulfurize the feed [8]. A wide-pore NiMo/ γ -alumina was tested for its performance in a vacuum residue hydroprocessing. The catalyst showed a remarkably high activity for HDM and asphaltene conversion reactions in the vacuum residue hydroprocessing [29].

Other than active metal and phase, pore size distribution has been found to affect the catalyst activity in hydroprocessing of vacuum residue. A hydroprocessing study using Kuwait vacuum residue as feedstock has shown that the effect of catalyst pore size was significantly different for different hydrotreating reactions [30]. Sulfided NiMo catalysts with unimodal and bimodal distributions with different proportions of meso- and macropores were prepared. For sulfur removal (HDS), a unimodal pore catalyst with maximum pore volume in the medium mesopore range (10–25 nm diameter) showed the highest activity. For HDM and HDN reactions, large-pore catalysts, having a major proportion of pore volume in 100–300 nm diameter pores, were found to be more effective.

2.4 Methods to create meso-/macro- and hierarchical pore system

γ - Al_2O_3 is the most commonly used support in catalysis for hydroprocessing. There are methods developed to prepare mesoporous and hierarchical texture support for hydrocracking catalyst. Two most important techniques for preparation of the material with the desired hierarchical texture are by hydrothermal and template methods.

2.4.1 Hydrothermal method

Hydrothermal method is an approach where the mixed solution (aluminum precursor, solvent, etc.) is poured into a sealed reactor. In the reactor, relatively high-temperature and high-pressure conditions promote the dissolution and recrystallization of poorly soluble or insoluble material. γ - Al_2O_3 is then produced by calcination of precipitated hydroxides [27, 31]. During the hydrothermal process, under the nonrestricted conditions, the crystal grows to its largest possible size, and its various characteristics such as shapes, high degree of crystallinity, uniform distribution, and

lighter particle agglomeration are developed [32]. The hydrothermal conditions such as water temperature, pressure, and viscosity of the solution are closely related to the development of the crystal morphology. The same type of crystal can be produced with different morphologies under different hydrothermal conditions [27, 33].

Stanislaus et al. [29] studied the mechanism of pore widening in γ -alumina under hydrothermal conditions in the presence and absence of additives such as P, F, phenol, and acetic acid. The formation and growth of boehmite into large crystallites by rehydration of γ -alumina were found responsible for pore enlargement. Li et al. [34] synthesized alumina from aluminum ammonium sulfate, urea, and polyglycol 2000 by hydrothermal method. It was reported that mesopore alumina of different morphologies can be fabricated merely by adjusting hydrothermal temperature.

2.4.2 Template method

Template method is a technology which is widely applied in recent years. It is a synthetic method for controlling the structure, particle size, and morphology of materials through utilization of a template [27].

Mesoporous alumina is normally prepared via surfactant templates. Su et al. [35] used $\text{Al}_2(\text{SO}_4)_3$ and NaAlO_2 as aluminum precursors for preparing lamellate structure mesoporous alumina with crystalline framework walls in the presence of non-ionic surfactant PEG6000. Well-crystallized mesoporous γ -alumina was formed after the samples were calcined at 600°C for 3 h. Mesoporous alumina prepared in this way exhibited a large surface area ($279 \text{ m}^2/\text{g}$) and a very rich porosity with large mesopores, and both the pore volumes and the pore sizes increased with the addition of the surfactant in the precipitation process [35].

Zhou et al. [36] used a promising strategy to prepare well-defined and uniform pore structure (WDUPS) Al_2O_3 by coating specially treated SiO_2 opals with Al_2O_3 . The pore size of the WDUPS Al_2O_3 was tailored in the range of meso- to macro-size by using microspheres of different sizes to fabricate the SiO_2 opal. When the SiO_2 opals were coated with optimal amount of Al_2O_3 , the obtained WDUPS Al_2O_3 showed a uniform acid density.

Recently, another hard template method, which uses polystyrene (PS) microspheres, was used to prepare a range of hierarchically porous alumina samples. The alumina precursor was mixed either with dry powder of PS microspheres (dry) or PS water suspension (wet) during preparation before pelletizing and calcination. The “wet” method gives pellets with a narrower distribution of macropores in size and the greater material mechanical strength. The approach allows tuning textural parameters of hierarchically porous alumina samples in different ranges of specific surface, mesopore volume, and total pore volume [37].

In a recent review by Galadima and Muraza [38] on hierarchical zeolites in hydrocracking catalysts, in general, the generation of the mesoporous zeolite systems could be achieved either during the initial crystallization process or through post-synthesis treatment processes. In either case, the resulting materials could have hierarchical arrangement of pore system or unimodal system. Another strategy adopted is the application of hard templates for synthesizing hierarchical zeolite. For achieving an efficient mass transport and high catalytic performance, the design of hierarchically porous catalytic supports is an interesting and most effective strategy.

3. Catalyst structure—activity relations

The catalytic activity is related to the structure of the catalyst. Daage and Chianelli [39] proposed the “rim-edge” model of MoS_2 for hydrotreating, in which

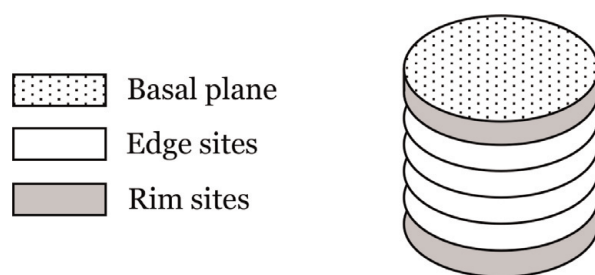


Figure 1.
Rim-edge model [39].

two kinds of exterior sites are responsible for hydrogenation (HYD) and hydrodesulfurization (HDS) (**Figure 1**). MoS₂ forms hexagonal or triangular slabs, and the rim sites around the exposed basal planes contribute to both HYD and HDS, and the exposed edge sites around the interior layers of MoS₂ stacks are accepted as active sites only in HDS.

The number of stacking layers of MoS₂ was then reported to increase the hydrogenation activity by promoting planar adsorption of aromatic rings on the edge sites [40]. Later, Lauritsen et al. [41] proposed the “brim site” model as the active site of HDS, based on observations of MoS₂ nanoparticles using scanning tunneling microscopy. The brim sites associated to Mo edges that are fully sulfided exhibit electron exchange capability as in typical metal catalysts.

In 2014, Chen et al. [42] compared the structure of hexagonal and triangular MoS₂ catalysts with their activities in hydrotreating. The hexagonal MoS₂ with more Mo edge sites was reported to have higher activity in HYD, but the triangular MoS₂ with more S-edge sites exhibited higher activity in HDS.

Similar catalyst structure-activity relations have also been found for W-based catalyst. In 2016, a DFT study that seeks to understand the active sites of “W-edge” or “S-edge” of NiWS phases showed that the surface concentration of “W-edge” and “S-edge” sites is closely related to the intrinsic hydrogenation activity of NiWS catalyst [43].

4. Recent advancement for heavy residue hydroprocessing

Low-quality heavy feedstock leads to quick catalyst deactivation, high coke formation, and large pressure drop in the operation of a fixed-bed reactor. In such a case, ebullated-bed or slurry-phase reactors can be an effective choice. These are systems designed with continuous addition and withdrawal of catalyst which allow one to control the catalyst deactivation due to coke formation as well as thermal exchanges in the reactor.

Supported catalysts are usually used in a fixed-bed or ebullated-bed reactor system for heavy oil hydroprocessing. On the other hand, nano-size unsupported dispersed catalysts are used in a slurry-phase reactor. In this case, the catalyst is in dispersed form such as unsupported metal particles, oil-soluble metals, or metal precursors that form in situ active phase during the process. Slurry-phase hydrocracking processes exhibit high selectivity and yield toward the product. For slurry-phase hydrocracking process of vacuum residue, both heterogeneous and homogeneous catalysts, depending upon the physical properties of the catalyst, are used. Catalyst development for heavy residue hydroprocessing is always ongoing for a better-performance catalyst and a longer catalyst run-length.

4.1 Supported solid catalyst

Carbon or carbon black has been tested as catalyst support for hydroprocessing. It is cheap and has a low tendency to form coke-related compounds (due to very weak acid sites). It has an affinity for V and Ni porphyrine-like compounds, which could be refrained from poisoning the catalyst by attacking the catalyst active sites. Meantime, it also has high HDS and HDN activities [44] and has no micropores below 3 nm which could be easily occluded, therefore turning active Ni and Mo metals into inactive ones [3]. However, carbon or carbon black supports are known for their low mechanical resistance since the structure of shaped catalyst particles easily collapses especially when used as catalyst in the ebullated-bed reactor [3]. To overcome the aforementioned mechanical resistance issue, a bimodal alumina modified with (8–18 wt%) carbon black composite support, containing 11–20% of total pore volume as macropores (>100 nm), was developed, and these prospective supports were impregnated with Ni and Mo. The addition of carbon black to alumina, after inert atmosphere pyrolysis, has produced strong shaped particles, suitable for high-colliding attrition applications, as commonly found in the ebullated-bed reactors. HDS and HDN can be enhanced when combining carbon black and macropores. It is also noted that catalysts containing macropores were reported more efficient in HDM than catalysts containing no macropores [3].

A series of mesoporous alumina catalysts with different textural properties were prepared by using the sol-gel method with the varied aluminum precursor, chain length of the surfactant, and calcination temperature. Mesoporous alumina with large surface area (270–380 m²/g) and pore size (3–19 nm) was successfully synthesized. The activity of mesoporous alumina-supported molybdenum catalysts with different properties in hydrocracking of residual oil was determined at 400°C. Higher conversion and higher liquid yield were achieved by using catalysts with larger mesopore size than catalysts with smaller pore size and similar acidity [45].

Dong et al. [46] synthesized a nest-like hollow γ -AlOOH microspheres constructed from numerous hierarchically organized nanowires via a template-free simple hydrothermal approach, from which hierarchically porous γ -Al₂O₃ microspheres with average macropores of 900 nm, mesopores of 20 nm, and a pore volume of 0.93 cm³/g were obtained readily. The nest-like γ -Al₂O₃ microspheres were tested as catalyst supports. The prepared MoNi/ γ -Al₂O₃ (hierarchically pore texture)-supported catalyst was applied for HDM catalysis. The catalysts exhibited superior catalytic performance and longer life due to enhanced diffusion of the reactants, compared to the catalysts prepared with the commercial γ -Al₂O₃.

A theoretical estimation of catalyst performance using geometrical characteristics of the porous media based on Monte Carlo methods and the graph theory was done on evolution of alumina catalyst texture during macromolecule conversion in heavy oil hydroprocessing [47]. In this study, a unimodal mesoporous structure of conventional catalyst and bimodal meso-/macroporous structure of the catalyst were modeled. Deactivation was modeled by the monotonic increase of alumina grain radius, which represented deposition of coke and metal species onto the surface of grains. There was a correlation observed for the hierarchical texture model and the experiment. Both the hierarchical texture in model and experiment were with prolonged catalyst lifetime.

A series of NiMoS/ γ -Al₂O₃ catalysts were prepared with varying Mo loading amounts, Ni addition, P addition, and porosity of γ -Al₂O₃ support, in order to design a suitable catalyst for hydrocracking of vacuum residue. Activity tests were conducted in an autoclave batch reactor at 420°C and 10 MPa H₂ in the presence of 0.26 wt% catalyst and 33.0 wt% tetralin. The amount of Mo loadings on γ -Al₂O₃ was observed most favorable at 8.0 wt% with the asphaltene conversion of 62.9%. The

addition of Ni had minimal effect on the vacuum residue hydrocracking but significant effect on the HDS activity. The increase in porosity of the γ - Al_2O_3 support reported to play an important role in enhancing the asphaltene conversion to 68.5% [48].

These metal-supported catalysts exhibit good performance in HDM, HDS, and hydrocracking reactions. However, when upgrading extra-heavy oil using these metal-supported catalysts, a critical problem of a short lifetime can result from deactivation of the active sites due to coke or sulfur deposition [14]. Hydrocracking processes that use heterogeneous catalyst of fixed-bed, ebullated-bed, or slurry reactors are always with the problems of feed diffusion, pressure drop, and mass transfer. The intraparticle mass transfer between liquid and solid phases, particle size, and mixing matter which must be taken into consideration [49]. All these concerns make limitations to feedstock used for the commercial application. Application of dispersed catalyst in slurry-phase hydrocracking is an alternate option to resolve these issues.

4.2 Unsupported dispersed catalyst

Coke formation resistance is vital to a hydrocracking catalyst since it determines the durability and lifetime of the catalyst. It is known that coke formation is markedly inhibited when the active species are applied as dispersed nanoparticle catalysts [14]. The application of the highly dispersed catalysts in the slurry-phase hydroprocessing of heavy residues favors the rapid uptake of hydrogen and deactivates the intermediate free radical moieties in the liquid phase, thereby suppressing coke formation, increasing total conversion, and enhancing quality of liquid product [50].

Dispersed catalyst can be classified into either water-soluble or oil-soluble [50]. Oil-soluble dispersed catalyst is generally preferred because it has a better catalyst activity as it can disperse uniformly in oil. To prepare oil-soluble dispersed catalysts, metals are usually introduced into the oil-soluble precursors to form an organometallic compound [1]. The metal precursors are then homogeneously dispersed in the reactor containing heavy oil or residue. The catalyst precursor will be activated (sulfided) in situ by reacting with the sulfur compound in the oil. Typical oil-soluble dispersed catalysts are such as molybdenum naphthenate and ammonium heptamolybdate [51]. For a water-soluble catalyst, pretreatments such as dispersion, emulsion, and dehydration are needed [1].

Catalyst or catalyst precursor and its dispersibility in the oil during the hydroprocessing of vacuum residue have direct correlation to the system performance. Among the transition metals, Mo- and W-based dispersed catalysts have been the focus of the study in hydrocracking of extra-heavy oils or vacuum residue. For instance, exfoliated MoS_2 was applied as a dispersed catalyst for Cold Lake bitumen upgrading [52].

In [52], the exfoliated MoS_2 , a two-dimensional MoS_2 material, was prepared via chemical exfoliation of MoS_2 particles that were dispersed in water. The results were compared with MoS_2 prepared in situ by the decomposition of molybdenum naphthenate. Although liquid yield and coke suppression were similar among those mentioned catalysts, a better hydrogenation activity, especially HDN, and asphaltene and microcarbon residue (MCR) removal were obtained with the exfoliated MoS_2 [52, 53]. The improved hydrogenation is believed to be a consequence of increased rim-edge sites [39] associated with the exfoliated MoS_2 .

In the case of using tungsten, unsupported nickel tungsten sulfide ($\text{NiWS}(x)$) particles, where x is the actual molar ratio of Ni/W ($x = 0, 0.005, 0.01, 0.02$), were applied as a dispersed catalyst for hydroprocessing of a vacuum residue (2.3 °API)

at 400°C with an initial H₂ pressure of 70 bar. Increasing the Ni content was found to increase the degree of sulfidation of tungsten, which promotes formation of Ni-W-S phases and enhances the overall catalytic activity. Among the NiWS(*x*) dispersed catalysts, the NiWS(0.02) catalyst showed the highest performance in total liquid product yield (87.0 wt.%), commercial fuel fraction yield (51.9 wt.%), and sulfur removal (86.5%) with coke formation (4.0 wt.%) suppressed efficiently [14].

Nano-sized tungsten carbide (2.8 nm) particles were synthesized using removable ceramic coating method and then were applied as dispersed catalysts to hydrocracking of vacuum residue, which was carried out at 400°C for 4 h with initial hydrogen pressure of 70 bar. The temperature programmed desorption analysis results showed that nano-sized tungsten particles are capable of superior hydrogen adsorption (compared to bulk tungsten carbide) as well as high catalytic performance, not only in commercial liquid yield (naphtha, middle distillate, and gas oil; 46.7 wt.%) but also in coke formation (5.9 wt.%) [20].

The effects of Co, Ni, or Mo precursors that have different oil solubility and oxidation state on the slurry-phase hydrocracking of vacuum residue at 400°C and 9.5 MPa H₂ were reported in [54]. The metal precursors were found to form nanoscaled dispersed particles of MoS₂, Co₉S₈, and Ni₃S₂, with the following vacuum hydrocracking performances in the order of MoS₂ > Co₉S₈ >> Ni₃S₂, based on the same metal loading of 0.113 mmol. Among the oil-soluble Mo precursors used, Mo-hexacarbonyl, Mo-octoate, and Mo-naphthenate, Mo-octoate has an intermediate oxidation state forms the smallest particles of 5.8 nm in size and exhibits the best activity in the vacuum hydrocracking.

Shin et al. [55] tested six newly synthesized metal precursors as catalysts for hydrocracking of vacuum residue. New group VI transition metal complexes, (LM(CO)₃) (M = Mo or W, L1 = 3-phenyl-1-propyne, L2 = 4-phenyl-1-butyne, and L3 = 5-phenyl-1-pentyne) were prepared by simply stirring M(CO)₃(RCN)₃ (R = Me, Et) in tetrahydrofuran solution. The catalytic activity was compared to the commercially available material, Mo-octoate. LMo(CO)₃ showed similar activities to Mo-octoate. Among all, L3Mo(CO)₃ which had the longest alkyl chain showed a comparable result of low yield for coke and gas products [55].

Different morphologies of oil-dispersed MoS₂ catalysts were obtained by a ligand stabilization method using Mo(CO)₆ as a Mo precursor and trioctylphosphine oxide as a coordinating agent to identify the active site of MoS₂ in the hydrocracking of vacuum residue. It was observed that the MoS₂ forms a nanoscaled monolayer from 5 to 10 nm in size. The effect of the oil-dispersed MoS₂ catalysts with different morphology on the slurry-phase vacuum residue hydrocracking process was investigated at 400°C and 9.5 MPa H₂. The turnover frequency (TOF), activity based upon the H₂ consumption rate per lateral metal number, of the dispersed MoS₂ catalysts in hydrocracking shows a good correlation with the rim-site Mo dispersion of the MoS₂ slabs based on the same metal loading of 0.113 mmol [56].

An oil-soluble W precursor, W(CO)₆, was used to prepare WS₂ in situ in the hydrocracking of vacuum residue, and its activity was compared to that of oil-dispersed MoS₂ prepared using the Mo precursor. Vacuum residue was treated in a batch reactor at 419°C at 9.5 MPa H₂ with the metal loading of 0.113 mmol. The TOF shows a higher value for WS₂ (0.709 s⁻¹) than MoS₂ (0.573 s⁻¹) catalyst. A higher asphaltene conversion for WS₂ (39.2%) than MoS₂ (35.8%) was obtained. These results suggest that the WS₂ catalyst exhibits a higher intrinsic activity than the MoS₂ catalyst in the residue hydrocracking process. It was noted that the dispersibility of WS₂ (58.0%) was found better than MoS₂ (3.3%) [17].

Liu et al. [57] proposed a simple method for the preparation of presulfided oil-soluble MoS₂ catalysts. The catalyst precursor, cetyltrimethylammonium heptamolybdate (CTATM), was synthesized by dissolving ammonium

tetrathiomolybdate in an aqueous solution containing excess cetyltrimethylammonium bromide, which could be directly dissolved in a vacuum residue. The obtained catalyst was evaluated in slurry-phase hydrocracking of vacuum residue at 410°C with an initial H₂ pressure of 10 MPa for 1 h. Remarkable hydrocracking activity was observed, with a reduction of the resin content from 25.21 to 3.54 wt% and of the C7-asphaltene content from 6.82 wt.% to almost zero. With using the catalyst, the liquid yield increased from 75.03 to 96.43 wt.%, coke yield and gas yield were 0.19, and 3.38 wt.%, respectively, significantly lower than the values of 14.05 and 10.92 wt.%, respectively, obtained without using the catalyst. Additionally, with increasing Mo content, HDM conversion increased from 42.5 to 83.4 wt%, while HDS conversion increased from 21.6 to 59.2 wt%. The CTATTM precursor shows good solubility and stability in heavy oil, leading to easy formation of small MoS₂ particles with stacking numbers of 1 and 2 and slab lengths of 5–11 nm. This presulfided oil-soluble MoS₂ catalyst shows a great potential for further industrial applications [57].

5. Catalyst deactivation

Hydrocracking of heavy oils differs markedly from that of light feeds owing to the fact that the catalysts used for this process are deactivated fast due to the presence of asphaltenes and metal containing molecules [58]. Restraining the deactivation of the catalysts is one of the main challenges in development of hydrocracking catalysts for heavy oil upgrading regardless of the reactor system chosen. A better understanding of the catalyst deactivation is one of the most important aspects to improve the catalytic performance in heavy oil and petroleum residue refining processes. A good commercial catalyst is known by its activity, selectivity, and stability.

The main causes of loss of activity in the catalyst are due to the formation of coke and deposition of undesirable carbonaceous products, metallic compounds, and asphaltenes on the catalyst surface. In addition, the structural changes including thermally or attrition of catalyst are also responsible for the deactivation [1].

In industrial catalytic processes, the loss of catalytic activity and/or selectivity over time is a major and continuing concern. The degree of catalyst deactivation is greatly influenced by the feed properties and the associated operating conditions. Generally, performance of catalysts decreases with time. In order to maintain constant product yields and/or quality, the loss of catalytic activity is compensated by periodic increases of reaction temperature [7]. Though significant costs, in the magnitude of billions of dollars annually, to industry are due to catalyst replacement and process shutdown, catalysts activity decay over time is unavoidable [59].

Catalyst deactivation is a complex process. Various model equations are developed in order to model the deactivation mechanisms such as coke deposition and metal accumulation. In the model, agents affecting the catalyst activity including metal content and coke precursors need to be taken into consideration. To achieve that, detailed characterizations of spent catalysts obtained at different reaction conditions, time on stream, and reactor position need to be carried out through various experiments. With the aforementioned information, a better deactivation model for heavy oil hydrocracking catalyst can be developed and further applied in reactor design, simulation, and optimization [59].

6. Conclusion

The key developments in better catalyst understanding in association with particle size, pore size distribution, and activity grading have greatly improved the

levels of conversion, increased run-length, and enhanced product qualities while maintaining residue fuel stability. Further catalyst performance improvement will likely come from catalyst optimization and better catalyst deactivation resistance resulting from metal poisoning and coke formation. The future challenge for a refiner will be to ensure a more efficient conversion of heavier feedstock to warrant a cleaner transportation fuel and sustainable environment for the generations to come.

Acknowledgements


Special thanks to Dr. Guan Tien Tan for his helpful comments, suggestions, and support while preparing the document.

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