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Hydroprocessing of heavy petroleum feeds: Tutorial

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1. Introduction

The world wide trends in crude oil supply indicate a declining availability of conventional crudes, which has been offset by increasing volume of heavy crudes. For the latter, the yield of liquid fractions can be increased by upgrading the distillation residues. A number of thermal processes (e.g., visbreaking, delayed-, fluid- and flexi-coking), so-called carbon rejecting processes, have been used on a commercial scale for several decades [1,2]. Heavy feeds can also be upgraded by hydroprocessing, so-called hydrogen addition option [3,4]. This requires the presence of hydrogen and an active catalyst. Compared with thermal processes, hydroprocessing operations are more flexible, giving higher yields of liquid fractions. An optimum of hydroprocessing operation can be achieved by properly matching the type of reactor and catalyst with the properties of heavy feeds. Several types of catalytic reactors, i.e., fixed-, moving- and ebullated-bed reactors are available commercially.

In spite of some similarities, hydroprocessing of heavy feeds differs markedly from that of light feeds. This results from the presence of high molecular weight asphaltenic molecules and organometallic compounds in the former. Then, the catalyst design has to take this fact into consideration. Special attention has to be paid to the textural properties of catalysts, such as pore diameter and pore volume. These parameters have to be optimized to ensure adequate surface area. The size and shape of catalyst particles are important for the efficient operation as well. An active catalyst for hydroprocessing of heavy feeds has to be resistant to deactivation by coke and metal deposits.

Because of so many parameters involved during preparation, the cost of catalysts used for hydroprocessing of heavy feeds is greater than that for the light feeds derived from conventional crudes. Significant efforts have been made to increase resistance of catalysts to deactivation, i.e., to prolong their life on stream. This involved modifications of the currently used catalysts as well as the development of the entirely new types of catalysts. The importance of the conditions applied during catalyst preparation and of the different supports on the catalyst performance has been recognized.

2. Properties of heavy feeds for hydroprocessing

Primary focus of this study will be on the heavy petroleum feeds containing high molecular weight hydrocarbons (asphaltenes and resins) and metals, predominantly in the form of porphyrines. At various degrees, such structures are present in atmospheric and vacuum residues derived from conventional and heavy crudes as well as from the bitumen obtained from tar sands. Rather extensive information on the properties of heavy feeds can be found in the literature [1,5–9]. Therefore, for the purpose of this study, a brief summary will only be given with focus on these properties which are important for hydroprocessing.

2.1. Composition of heavy feeds

Table 1 shows the yields of atmospheric (>345 °C) and vacuum (>565 °C) residues from well known crudes [10]. Choice between the atmospheric and vacuum residue for the subsequent hydroprocessing depends on the operating strategy of a refinery. The parameters which are relevant for hydroprocessing are shown in Table 2. These results indicate a great variation in the properties of heavy feeds. A simple parameter such as molecular H/C ratio exhibits a decreasing

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Table 1
Yields of atmospheric (>345 °C) and vacuum residues (>565 °C) as volume% of crude [10]

Crude	Yield of AR (>345 °C)	Yield of VR (>565 °C)
Arabian Light	44.6	14.8
Arabian Heavy	53.8	23.2
Maya	56.4	31.2
Boscan	82.9	–
Cold Lake	83.1	50.0
North Slope	52.6	18.0
Torrey Canyon	48.4	36.0
Kuwait Export	45.9	21.8
Ekofisk	25.2	13.2

trend from light crudes toward heavy crudes. A similar decreasing trend is observed starting with light fractions towards heavy fractions and residue derived from the same crude [11], i.e., from about 1.9, 1.7 and 1.4 for a naphtha fraction, gas oil and vacuum residue, respectively. The complexity and/or difficulties, as well as hydrogen requirements and severity of the operating conditions applied during hydroprocessing increase in the same direction.

Heavy feeds can be described as the colloidal solution consisting of three fractions in the increasing order of the average molecular weight, i.e., oils, resins and asphaltenes. Asphaltenes, as the heaviest fraction, represent a group of large molecules separated from the feed by precipitation using paraffinic hydrocarbons such as pentane, hexane and heptane. Essential parts of the heavy feeds are micelles which are dissolved in the oil fraction. Micelles are aggregates of asphaltenes and resins held together by weak physical interactions. Asphaltenes occupy the core of the micelles with resins being adsorbed on the external surface and as such act as a dispersing agent for asphaltenes. Resins are less polar than asphaltenes but more polar than oil. This ensures an equilibrium between the micelles and the surrounding oil fraction as well as the homogeneity of the colloidal system. Without resins presence, asphaltenes would coagulate and form sediments during storage and transportation. It is essential that during hydroprocessing, resins are converted at a similar rate as asphaltenes. Otherwise, a much greater rate of the conversion of resins than that of asphaltenes would result in the incompatibility of the components of the colloidal system. This would lead to the coagulation of the asphaltenes resulting in sediments formation on the catalyst surface.

Attempts have been made to develop models depicting the structure of asphaltenes and resins [1,5–9]. This usually involves an extensive fractionation of a heavy feed, followed by detailed characterization of the isolated fractions. A number of structural parameters of the fractions can be determined using ^{13}C and ^{1}H NMR spectroscopy, whereas the organic groups present can be identified by FTIR spectroscopy. This approach was used by Suzuki et al. [8] for the model development of Athabasca bitumen. The asphaltene dimer proposed by these authors is shown in Fig. 1 together with hypothetical structures of Maya [12] and Venezuelan crudes [13] asphaltenes. It is obvious that the latter are more complex than Athabasca bitumen. The model of Athabasca asphaltenes is used to depict some of the reactions occurring during hydroprocessing. First of all, the cleavage of weak bonds, identified by a broken lines and numbers may proceed hydro-thermally, not requiring an active catalyst. It is obvious that site 1 will cleave first. In fact, this may take place in the feeding lines and/or during preheating the feed. The cracking of sites 2 will be more favorable in the positions more distant from the aromatic ring. Naphthenic rings (site 3), though more stable than methylene bridges, represent another potential cracking sites. The low reactivity of the remaining predominantly aromatic residue is the main reason for rather severe conditions applied during hydroprocessing of heavy feeds. Thus, without a high H_2 pressure and an active catalyst present this residue would convert to coke.

2.2. Metals in heavy feeds

V and Ni are the predominant metals in petroleum crudes, heavy oils and bitumen derived from tar sands. The content of V and Ni varies between few ppm to several 1000 ppm. With few exceptions, the content of V is greater than Ni. To a various degrees Fe, Ti, trace metals and small amounts of other metals can also be present in addition to clay-like mineral matter [14]. A de-watering and/or desalting of some crudes may be required to remove alkali metals which are usually in the form of chlorides and bromides.

From the hydroprocessing point of view, the presence of V and Ni has been attracting most attention [15,16]. Several forms of V and Ni containing porphyrins have been identified in heavy feeds [17,18]. It was suggested that porphyrins account for only about half of V and Ni in crudes [19]. The unaccounted part was supposed to comprise less defined forms which may involve some bonding with heteroatoms. Indeed, the size exclusion chromatography technique used by Sughrue et al. [20] revealed

Table 2
Properties of atmospheric (AR) and vacuum (VR) residues from various crudes

Properties	Kuwait VR	Arab Heavy VR	Maya VR	Maya AR	Venezuela AR
Yield (wt.%)	30.5	39.4	37.1	61.0	48.9
Specific gravity (kg/L)	1.021	1.023	1.0644	1.0068	0.9509
Sulfur (wt.%)	5.35	5.10	5.7	4.76	1.78
Asphaltenes (wt.%)	15.4	20.0	26.3	13.16	–
Nickel (wpm)	33	40	127.19	78.45	25
Vanadium (wpm)	87	142	684.0	436.64	185
Viscosity (cSt)	1105	1540	–	–	–

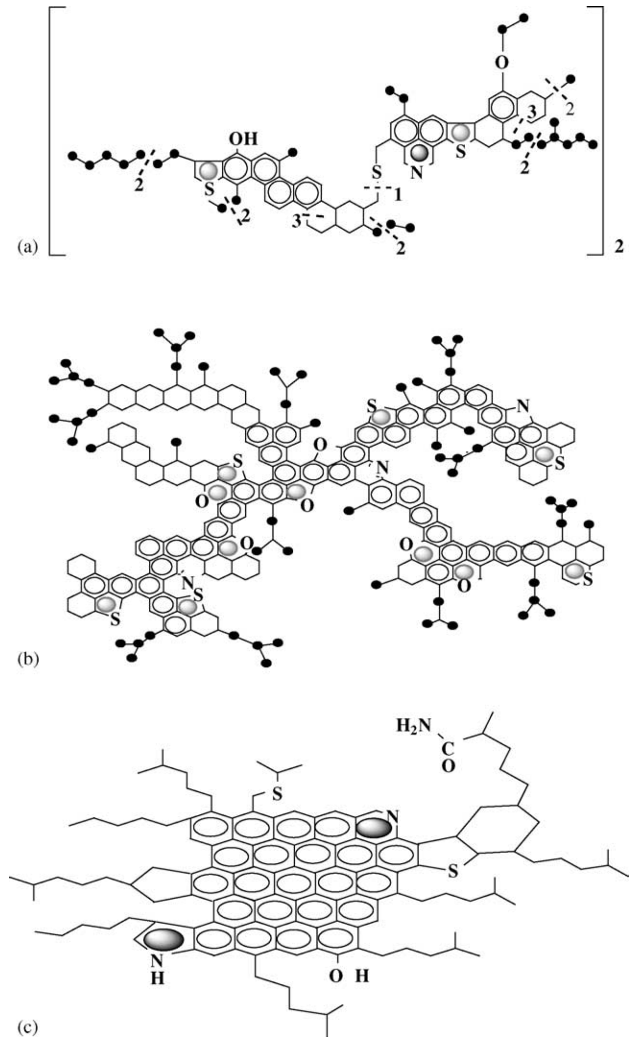

Fig. 1. Molecular structure of asphaltenes derived from (a) Athabasca bitumen [8], (b) Maya crude [12], and (c) residue of Venezuelan crude [13].

the presence of large and small V molecules. The latter disappeared after hydroprocessing of the feed. At the same time, the large molecules were more resistant. It is suggested that the large V containing molecules were associated with asphaltenes, most likely in a porphyrin-like form because asphaltenes were not completely removed from the feed. This was indeed confirmed by Sakanishi et al. [21] who observed that porphyrins may be occluded by a strong non-covalent interaction as part of the asphaltenes aggregates. Once porphyrins were released from the aggregates, i.e., by an interaction with a solvent, a molecular weight typical of porphyrins was approached. This observation was further supported by Grigsby and Green [22].

Hydroprocessing of V and Ni containing porphyrins involves a hydrogenation equilibrium between the porphyrin and the corresponding chlorin shown in Fig. 2 [23]. Apparently, this step does not require the presence of catalyst if a sufficient H_2 pressure is maintained. Hydrogenation of at least one pyrrole ring induces significant flexibility in the macro-cyclic ligand [19]. This diminishes the stability of the transition complex. The final step in the HDM of porphyrins involves the cleavage of a metal–N bond. This step is essentially hydrogenolysis and requires the presence of a catalyst. During hydroprocessing, the deposition of V on catalyst occurs at much greater rate than that of Ni. Then the HDM of V containing porphyrins may have an adverse effect on the removal of Ni.

2.3. Physical properties

Viscosity appears to be the most important physical property of heavy feeds. A sufficiently low viscosity has to be maintained to ensure adequate pumpability. Fig. 3 shows that the viscosity of a crude depends on the amount of the >350 °C residue and/or the yield of <350 °C distillate [24,25]. At ambient temperatures, heavy crudes and distillation residues (vacuum residues in particular) are in a semi-solid form. In this form, their pumpability is rather low. Increasing temperature leads to decrease in viscosity because of a gradual change in the colloid structure of semi-solids. This results from the increased mobility of micelles in oil fraction. In refinery practice, the need for reheating heavy feeds is avoided by integrating distillation units with catalytic reactors. This ensures that distillation residues, while still possessing sufficiently low viscosity are fed directly to a reactor for hydroprocessing. For heavy crudes, upgrading has to be performed on site with the aim to achieve sufficient pumpability for pipelining. According to the commonly accepted rule, the viscosity should be lower than 120 cSt at 20 °C, whereas in the southern hemisphere a greater viscosity can be tolerated [25]. Blending a heavy crude and/or a heavy feed with a lighter fraction may be another option for achieving a desirably low viscosity. However, in this case, it is essential that the blended materials are compatible. Otherwise, the sediments formation cannot be avoided [26].

Fig. 3 [24] suggests that there might be a correlation between viscosity, as well as CCR and asphaltenes content. However,

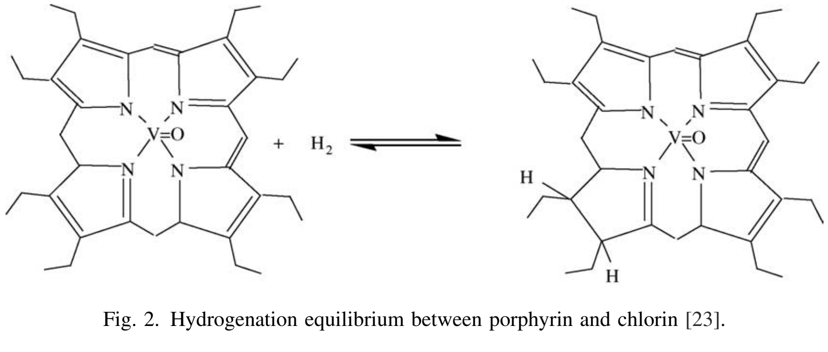

Fig. 2. Hydrogenation equilibrium between porphyrin and chlorin [23].

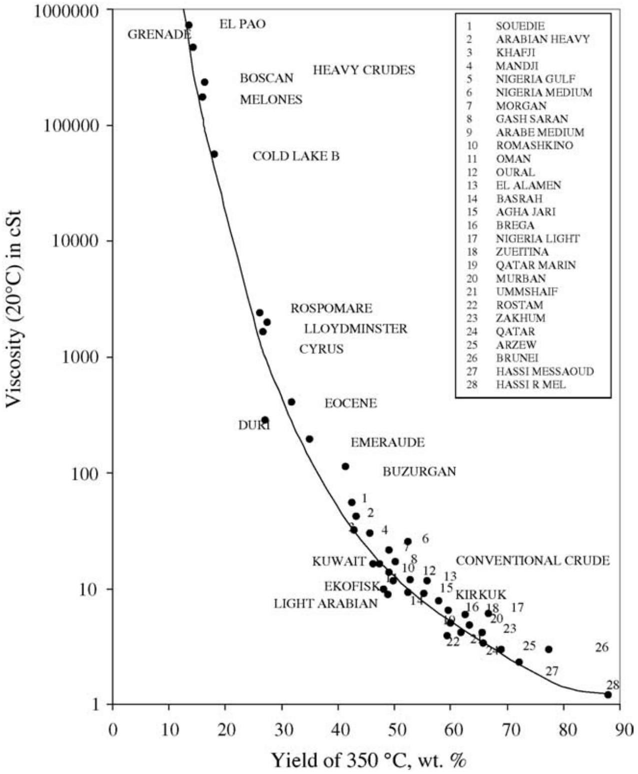

Fig. 3. Viscosity of crude vs. yield of <350 °C fraction [24].

after closely examining an extensive database, a rather poor correlation could be established. There is no correlation between viscosity and specific gravity. Thus, feeds varying widely in viscosity may have similar specific gravity. This is not surprising because different factors are involved in determining the values of viscosity and specific gravity.

3. Properties of catalysts for hydroprocessing of heavy feeds

The bibliography on the properties of hydroprocessing catalysts is rather extensive and has been the subject of a number of reviews [27–31]. A special attention was devoted to the hydrogen activation without which hydroprocessing reactions could not proceed [32]. Detailed account of the methods used for the catalyst preparation was given as well [33–36]. It is well established that during hydroprocessing, the catalyst activity declines. At certain point, catalyst has to be replaced and sent either for regeneration or disposal. Extensive reviews on deactivation [15] and regeneration [37] of hydroprocessing catalysts were also published. It has been shown that the safety, utilization and disposal aspects of spent hydroprocessing catalysts require special attention [16].

It is again stressed that the design of catalysts for hydroprocessing of heavy feeds has to take into consideration the presence of high molecular weight compounds (e.g., asphaltenes and resins), as well as heteroatom (S, N and O) containing structures and metals such as V, Ni, Fe and others. This suggests that a high activity of catalyst must be complemented by an adequate tolerance to metals. A wide range of heavy feeds available suggests that tailor-made catalysts suitable for a particular feed may need to be designed. In this regard, both chemical composition and physical properties of catalysts require special attention. Moreover, the size and shape of catalyst particles must be matched with the properties of feed and type of catalytic reactor.

3.1. Chemical composition

It is evident that all aspects of hydroprocessing catalysts have been reviewed in details [15,16,27–37]. Therefore, a brief and general account of chemical composition will only be given with emphasis on the conventional hydroprocessing catalysts. Among those, the Mo-containing supported catalysts, promoted either by Co or Ni have been used for hydroprocessing for decades. The γ-Al_2O_3 has been a predominant support, however, silica–alumina and zeolites were also used with aim to enhance rate of hydrocracking reactions. The operating (sulfided) form of catalysts contains the slabs of MoS_2. The distribution of slabs on the support, i.e., from a monolayer to clusters, depends on the Mo loading and sulfiding temperature. The unsupported MoS_2 exhibits a hexagonal coordination. It is reasonable to assume that the same coordination will be retained in the supported catalysts. Under hydroprocessing conditions, the corner and edge sulfur ions in MoS_2 can be readily removed. This results in the formation of the coordinatively unsaturated sites (CUS) and/or sulfur ion vacancies which have Lewis acid character. Double and even multiple vacancies can be formed. Because of Lewis acid character, CUS can adsorb molecules with unpaired electrons, e.g., pyridine.

The promoters such as Co and Ni decorate MoS_2 crystals at the edge sites of the slabs. In the presence of Co or Ni, CUS are considerably more active than those on MoS_2 alone. The H_2S/H_2 ratio is a critical parameter for maintaining optimal number of CUS. The presence of -SH groups possessing a Brønsted acid character has been confirmed [38]. Apparently, hydrogen activation required for hydroprocessing reactions occurs on CUS. This involves a homolytic and heterolytic splitting of hydrogen leading to the formation of Mo-H and -SH groups, respectively. These groups are the source of hydrogen for hydroprocessing reactions, which are based on the transfer of hydrogen to reactant molecules adsorbed on CUS. A prolonged adsorption of reactants, e.g., N-containing species on CUS may slow down hydrogen activation process and eventually lead to catalyst poisoning [33,39]. Furthermore, the formation of coke and metal deposits on CUS will diminish the availability of active site. The loss of catalyst activity during hydroprocessing of heavy feeds will be caused mainly by coke and metals [15].

During the operation, the oxidic form of the catalysts is converted to a sulfided form. For hydroprocessing of heavy feeds, an operating time may be gained if the catalyst sulfiding is performed prior to contacting the feed. In this case, a decreased catalyst deactivation is expected. Presulfiding can be performed either in situ or ex situ. Practical experience suggests that the ex situ presulfiding yield more active catalyst. Fig. 4 shows that the ex situ (actiCAT) process is rather simple compared with the in situ presulfiding [40–42].

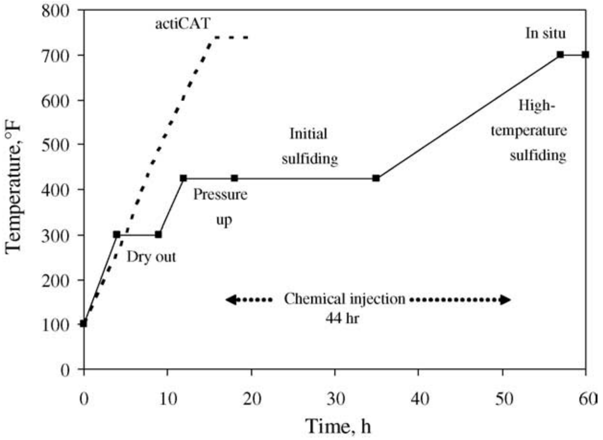

Fig. 4. Comparison of the ex situ and in situ presulfiding [41].

It has been shown earlier that properties of supports are crucial for defining the desirable porosity of catalysts. However, the catalyst performance can also be modified by chemical composition of supports. It is well established that additives such as phosphate, fluoride, boride, etc., can modify Al_2O_3 support and eventually improve catalyst activity, though in some cases, little effect on activity was observed [43]. Supports consisting of bi- or even multiple-oxides have been evaluated but predominantly in various model feed studies [44]. Beneficial effects of such supports resulted from the improvement of acidic sites distribution. This, in turn improved hydrocracking activity which is required for achieving a desirable conversion of asphaltenes and resins to distillate fractions. This was indeed confirmed by Corma et al. [45] who compared the conventional NiMo/γ-Al_2O_3 catalyst with a series of the NiMo catalysts supported on amorphous silica–alumina and several different zeolites. At the same time, more acidic supports had an adverse effect on other catalyst functionalities. Therefore, the activity of catalysts for hydroprocessing of heavy feeds must be optimized to achieve a desirable level of hydrocracking simultaneously with that of HDM, HDS and HDN. In this regard, Maity et al. [46] showed that the catalyst functionalities can be modified by incorporating about 5 wt.% of TiO_2 into Al_2O_3. In this case, pore volume and mean pore diameter of catalysts could be controlled by the addition of TiO_2 to Al_2O_3. Catalysts supported on carbon are less sensitive to poisoning by N-bases, however, their hydrocracking activity may be low unless the carbon support is subjected to special pretreatments. Fig. 5 shows that catalysts supported on basic supports (e.g., MgO-Al_2O_3, ZrO_2-Al_2O_3) were slightly more stable and more selective for HDM than TiO_2-Al_2O_3 supported catalyst [47,48]. This was attributed to small amounts of MgO, ZrO_2 and TiO_2 (7.2, 9.2 and 9.0 wt.%, respectively) added to γ-Al_2O_3. Initially, the TiO_2-Al_2O_3 supported catalyst was more active because of its higher acidity. However, the use of catalysts supported on basic supports in hydroprocessing of heavy feeds may be limited because their HYD and hydrocracking activities are low.

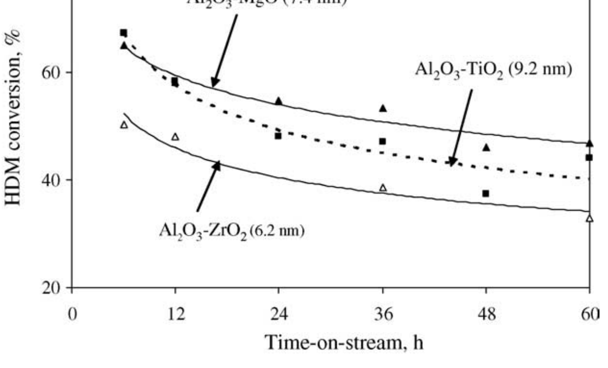

Fig. 5. Effect of the nature of catalyst support on HDM conversion [47,48].

3.2. Physical properties

Textural properties such as pore volume and pore size distribution and mean pore diameter have to be optimized to maximize catalyst utilization. Fig. 6 illustrates the difference in pore mouth plugging between small and large pores. The pore size distribution of fresh and spent catalysts are presented as relative area of nitrogen adsorption–desorption isotherms for two different mean pore diameter catalysts along the deactivation on the pore mouth. The increases in hysteresis loop were considered as representative of deactivation by pore mouth coking [49]. In the case of fresh catalysts, the pores are considered cylindrical whereas for spent catalyst the pores are "*ink-bottle*" types due to metal and carbon deposition which resulted in an increase in area of hysteresis loop. A high surface area and moderate pore volume catalysts are very active for HDS because of the efficient dispersion of active metals in

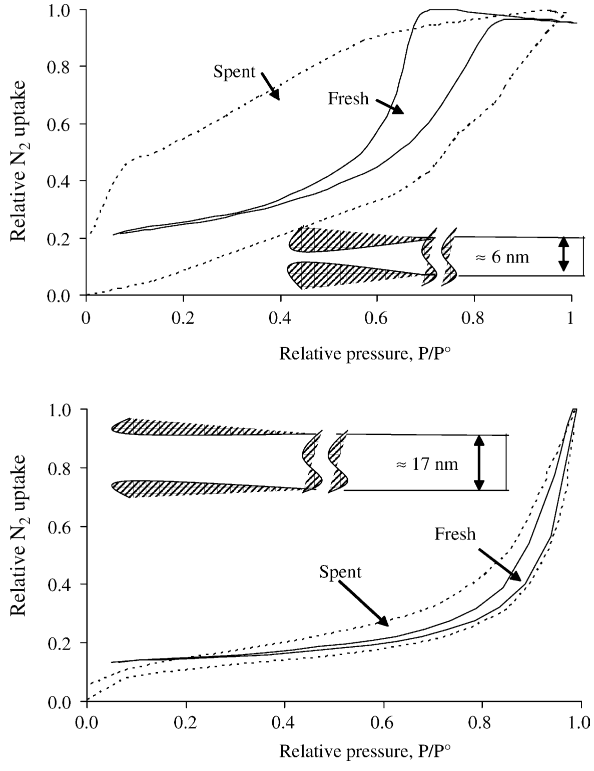

Fig. 6. Fresh and spent catalysts adsorption–desorption isotherms. (a) CoMo/γ-Al_2O_3 (6 nm average pore diameter) and (b) CoMo/γ-Al_2O_3 (17 nm average pore diameter) [49].

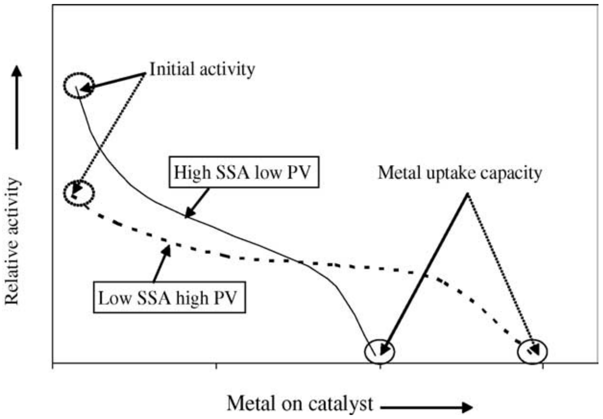

Fig. 7. Relationship between catalyst activity and metal accumulation [50] (SSA: specific surface area, PV: pore volume).

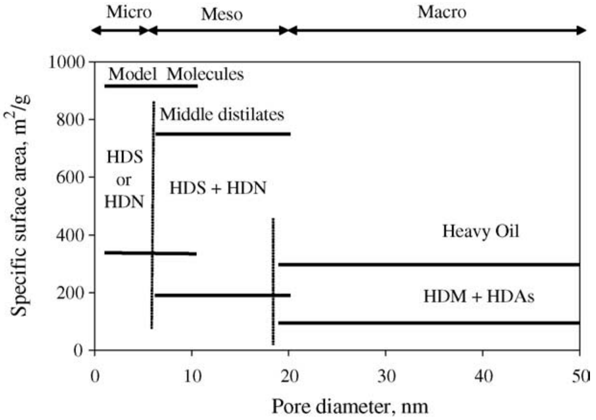

Fig. 8. Effect of pore diameter and specific surface area on hydrotreating catalyst activities.

pores. However, in case of heavy feeds, these pores become gradually unavailable because they are deactivated by pore mouth plugging. On the other hand, catalysts with a small surface area and large pore volume are less active because of a lower concentration of active sites. However, they are more resistant to deactivation by pore mouth plugging and their metal storage capacity is greater. The effect of surface area and pore diameter and/or pore volume on catalyst deactivation and their applicability are shown in Figs. 7 and 8, respectively [50].

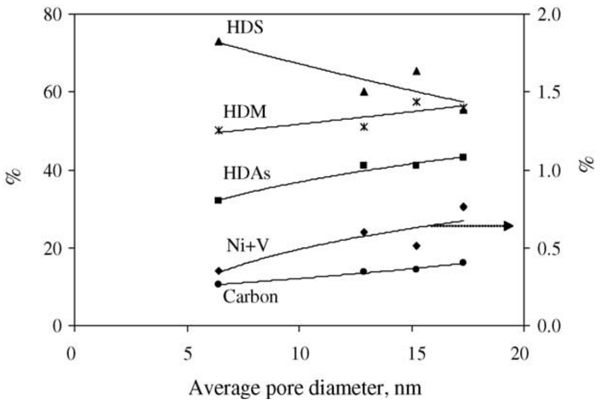

Fig. 9. Effect of average pore diameter on conversion after 60 h time-on-stream, and deposition of carbon and metals [51].

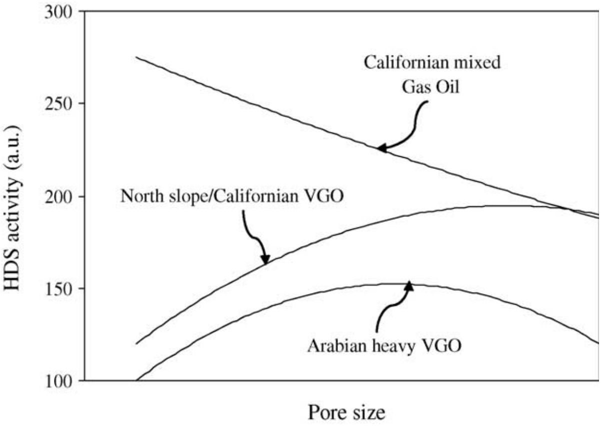

Fig. 10. Effect of feed origin and pore size on catalyst activity [54].

Different activities and capacity for carbon and metal depositions are shown in Fig. 9 [49,51] as function of average pore diameter (APD). Opposite trends in HDS and HDM activities suggest that HDM catalyst should be macro-porous. This is indicated by low HDM conversion for a low APD catalyst caused by restricted diffusion of large metal-containing molecules (porphyrins and/or metal chelating compounds) into the pores. The parallel increase in HDM and hydrodeasphaltization (HDAs) conversions indicate that these functionalities are dominated by catalyst pore structure, whereas an efficient dispersion of active phase is essential for achieving a desirable HDS activity [52]. Therefore, factors which are important for HDS activity differ from those which dominate HDM and HDAs activities [50,53].

The above discussion suggests that there is an optimal combination of surface area and pore diameter giving the highest catalyst activity. The optimum may be different for different feeds and catalysts. This is clearly demonstrated in Fig. 10 showing that the optimal pore size to achieve the highest activity during the HDS of the heavy feed differed from those required for the lighter feeds [54]. Similarly, the effect of porosity on catalyst performance was confirmed during hydroprocessing of an atmospheric residue and a heavy gas oil over a microporous conventional HDS CoMo/Al_2O_3 catalyst [51]. As Fig. 11 shows, for the latter, steady catalyst

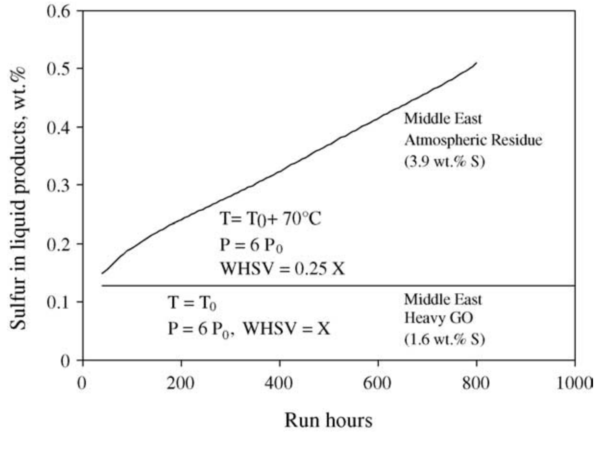

Fig. 11. Effect of feed origin on HDS (standard CoMo catalyst) [53].

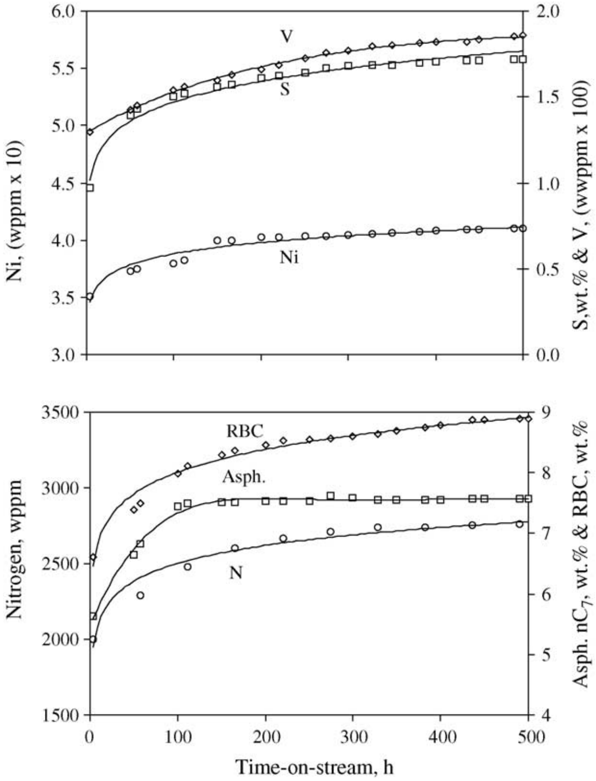

Fig. 12. Time-on-stream vs. properties of hydrotreated heavy oil [55] (RBC: Ramsbottom carbon).

performance was maintained for an extensive period, whereas a continuous catalyst deactivation was observed during hydroprocessing of the atmospheric residue. For the latter, the catalyst was deactivated by both coke and metal deposits. It is well established that the initial rate of coke formation is high and then gradually attains a steady state. On the other hand, the formation of metal deposits is almost linear with time on stream, as it is indicated by a more gradual increase in metal content in products shown in Fig. 12 [55].

Table 3
Distribution factors for V and Ni [57,58,60]

Catalyst	MPD[a]	Θ for vanadium		Θ for nickel	
		Heavy Arab >454 °C	Maya >454 °C	Heavy Arab >454 °C	Maya >454 °C
A	2.7	0.82	0.68	–	0.77
B	–	0.76	0.64	0.89	0.74
C	2.3	–	0.47	–	0.55
D	1.8	–	0.36	–	0.41
E	1.3	0.41	–	0.56	–
F	1.0	0.30	–	0.34	–
G	0.7	0.13	–	0.17	–

[a] MPD: mean pore diameter (relative scale).

An optimal pore size and volume distribution is critical for hydroprocessing of high metal content feeds. This results from a large molecular diameter of V- and Ni-containing porphyrin molecules. For small pore diameter, most of metals will deposit on the external surface of catalyst particles and the diffusion into the catalyst interior becomes a rate-limiting factor. It is, therefore, expected that the tolerance of catalyst to metals will increase with increasing pore diameter as it is shown in Fig. 13 [56]. At the same time, the catalyst activity will decrease. At a certain pore radius, the tolerance to metals abruptly decreased, whereas the activity decrease is less pronounced. To a certain extent, these phenomena can be quantified by the distribution factor (Θ) defined as:

$$\Theta = \frac{\int M(r)\mathrm{d}r}{M_{\max}\int r\mathrm{d}r} \tag{1}$$

where $M(r)$ is the local concentration of metal deposits in the catalyst particle, r the fractional radius and $M_{\max}$ is the concentration of metals at the maximum [57]. The Θ values approaching 1.0 indicate and even distribution of metal across particles, whereas the value approaching 0 suggests that metals deposit preferentially on the external surface of catalyst particles. The effect of pore diameter on distribution factor is shown in Table 3. It was determined that catalyst life increased with increasing distribution factor [57,58].

Attempts have been made to develop correlations between distribution factor and catalyst properties. A correlation in Fig. 14 shows that for the same surface area, it is more advantageous to use bimodal catalysts compared with unimodal catalysts [59]. The former catalysts contain different fractions of micro, meso and macro pores and can be tailor-made to suit hydroprocessing of various feeds. Because of a higher metal tolerance, bimodal and even polymodal catalysts have a longer

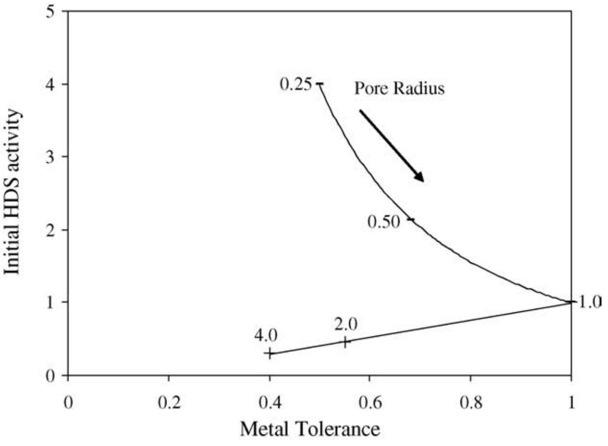

Fig. 13. Effect of pore radius on activity and metal tolerance [56].

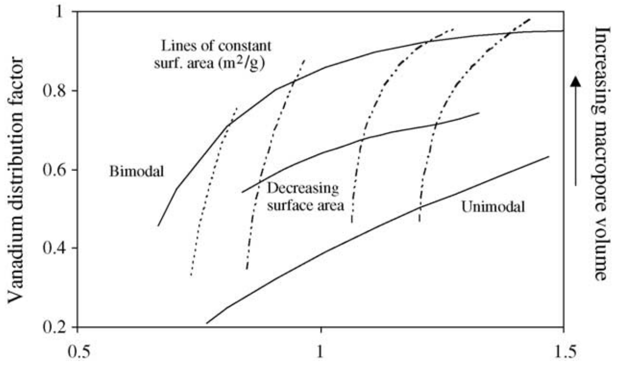

Fig. 14. Effect of textural properties of catalyst on distribution factor [59].

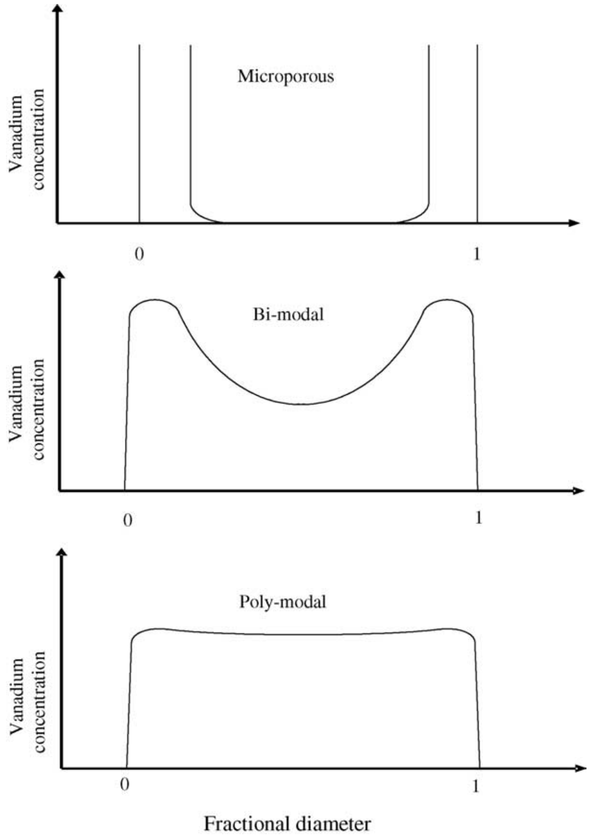

Fig. 15. Effect of the type of porosity on radial distribution of vanadium [62].

life and their metal storage capacity may approach 100% of the original catalyst weight. For example, the metal storage capacity of a macroporous NiMo catalyst supported on a ‘‘chestnut burr’’ like Al_2O_3 exceeded 100% of the original catalyst weight [61]. As it is shown in Fig. 15 [62], for bimodal catalysts with a large fraction of macropores, the radial distribution of metals is more even compared with a microporous unimodal catalyst. An ideal case of the metal distribution represents a polymodal catalyst providing that an optimal combination of the activity and porosity of the catalyst can be attained.

3.3. Mechanical properties

Catalyst particles must posses an adequate mechanical strength to ensure a smooth operation of a catalyst bed. This is much more critical for heavy feeds than for light feeds. Thus, it is more difficult to maintain a desirable mechanical strength for macroporous catalysts than that for microporous catalysts. In the case of fixed bed reactors, cracking the particles (because of the insufficient mechanical strength) can lead to the unwanted phenomena such as pressure drops along the catalyst bed, creation of channels causing the mal-distribution of feed and even a collapse of fixed bed resulting in an unexpected shutdown of the operation. A similar malfunctioning of catalyst bed can be experienced with the catalyst particles possessing an insufficient resistance to attrition. The mechanical properties of catalyst can be controlled during the preparation. In this regard, both the selection of a suitable binder as well as an optimal temperature and duration of catalyst roasting are important. Furthermore, methods used for the addition of active metals to the catalyst support can play certain role as well [36,37]. In the published articles, the importance of mechanical properties on the catalyst performance has been frequently underestimated.

3.4. Shape and size of catalyst particles

In spite of the significant advancements in catalyst development, the diffusion problems encountered during hydroprocressing of heavy feeds cannot be entirely eliminated. In this regard, the size of catalyst particles is another parameter deserving attention. For large particles, a near center part may not be utilized even for a macroporous polymodal catalyst. To a certain extent, this can be overcome by decreasing the diameter

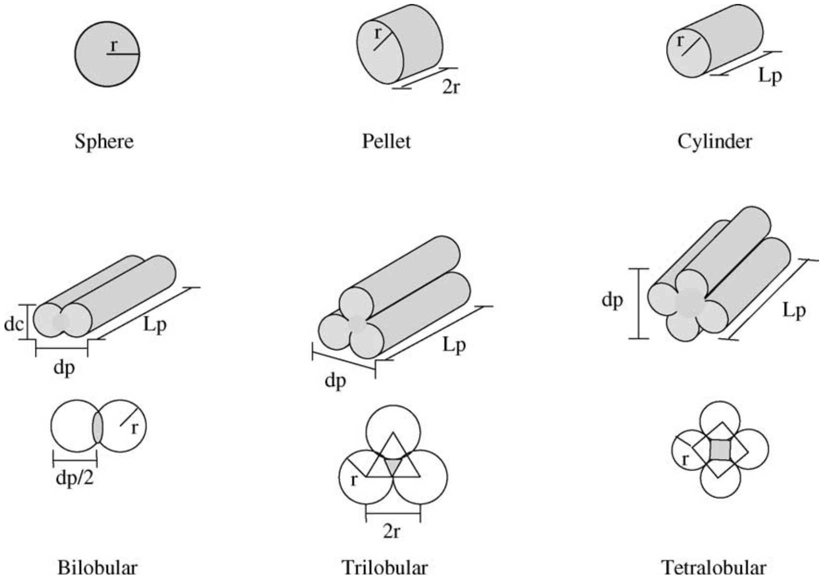

Fig. 16. Particle shapes of industrial hydroprocessing catalysts [63].

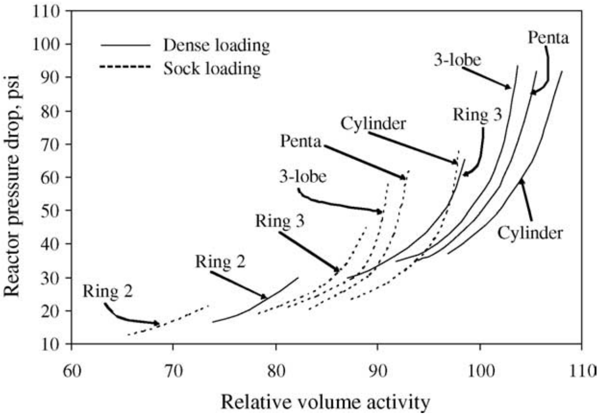

Fig. 17. Effect of catalyst shape and loading on reactor pressure drop and activity [64].

of particles. But, there may be a limit to the diameter after which particles desintegrate. Apparently, this limit is approached when the outside diameter of particles is about 0.8 mm (1/32). However, such small particles may not be suitable for fixed bed reactors because of large pressure drops. This can be overcome by selecting a proper shape of particles. Some shapes of particles which may be suitable for hydroprocessing of heavy feeds are shown in Fig. 16 [63]. Fig. 17 demonstrates that for both the dense and sock loading of catalyst, a selection of an optimal size and shape of particles is crucial for the performance of a fixed bed. The optimal matching of the particles shape with different types of catalytic reactors will be discussed latter in the review.

The activity of a catalyst, having the same chemical composition and structure depends on the size and shape of its particles. For this purpose, Cooper et al. [64] defined the size of catalyst particles (L_p) as:

$$L_\mathrm{p} = \frac{V_\mathrm{p}}{S_\mathrm{p}} \tag{2}$$

where V_p and S_p are the external particle volume and geometric surface area, respectively. Results of these measurements are shown in Table 4. The activity for HDS of a heavy oil was determined for an equal catalyst weight basis. The trends indicate an improvement in catalyst performance with the decreasing particle size. It was established [65] that L_p correlated with Thiele modulus (Φ_L) defined as:

$$\Phi_L = L_\mathrm{p}\left(\frac{k_\mathrm{i}C^{n-1}}{D_\mathrm{eff}}\right)^{0.5} \tag{3}$$

where k_i is the intrinsic rate constant, C the concentration of reactant, n the reaction order and D_eff the effective diffusivity defined as $D_\mathrm{eff} = D_\mathrm{b}\theta/\tau$, where θ and τ are the porosity and tortuosity of a catalyst, respectively, and D_b is the bulk diffusivity. The detail of the effects of these parameters on catalyst performance, particularly its deactivation during hydroprocessing of heavy feeds was given elsewhere [16].

Table 4
Effect of particle size and shape on HDS activity [64]

Shape	Dimensions (mm)	$V_\mathrm{p}/S_\mathrm{p}$ (mm)	Activity
Cylinder	0.83 o.d. × 3.7 L	0.189	9.7
Cylinder	1.2 o.d. × 5.0 L	0.268	7.9
Cylinder	1.55 o.d. × 5.0 L	0.345	5.7
Ring	1.62 o.d. × 0.64 i.d. × 4.8 L	0.233	8.7
Ellipse	1.9 o.d. × 1.0 i.d. × 5.0 L	0.262	8.4
3-Lobe	1.0 o.d. × 5.0 L	0.295	8.2
Crushed	0.25–0.45	~0.04	14.0

o.d.: outside diameter, i.d.: inside diameter, L: length.

3.5. Catalyst life

Because of the additional factors involved during manufacturing, the cost of catalysts for hydroprocessing of heavy feeds is significantly greater than that for hydroprocessing light feeds. Therefore, the extending the life on stream as much as possible is the main objective of the studies on design and preparation of catalysts for hydroprocessing of heavy feeds. This is carried out simultaneously with testing catalysts to identify optimal operating parameters for a heavy feed of interest. Attempts have been made to develop models for predicting long time performance of catalysts. Significant savings in time and cost can be realized by selecting an optimal catalyst formulation and by simulating commercial operations using models.

Models focus on the initial deactivation by coke deposition followed by a steady state coke build-up on the catalyst surface. They also have to take into consideration a more or less linear and continuous deposition of metals from heavy feed. Models incorporate interphase, intraphase and interparticulate gradients of temperature and concentration. A mathematical form of a model obtained by combining chemical and physical laws can be solved to obtain data for predicting reactor performance. The validity of models can then be verified using data on accelerating aging of catalysts obtained in pilot plants together with data obtained in commercial units. After the validation, models can be used for selecting an optimal catalyst for hydroprocessing of a particular feed. Sometimes, a model is developed to simulate a specific catalytic process.

Several models have been used to simulate hydroprocessing operation involving heavy feeds. The modeling studies of Hannerup et al. [17,66] stressed the importance of combined effects of diffusion and activity on reaction rate. Thus, for a given process and heavy feed, a catalyst possessing an optimum particle shape and size as well as suitable porosity can be identified by models. Also, these authors observed that H_2S/H_2 ratio is another important parameter to be considered. The model developed by Reyes et al. [67] could predict catalyst life during the HDM of a deasphalted feed containing more than 230 ppm of V + Ni. Among four catalysts varying in porosity, the one exhibiting highest performance could be identified by model. Similarly, Takatsuka et al. [68] used three different catalysts for hydroprocessing of a heavy feed containing more than 260 ppm of V + Ni. As Fig. 18 shows, their model could

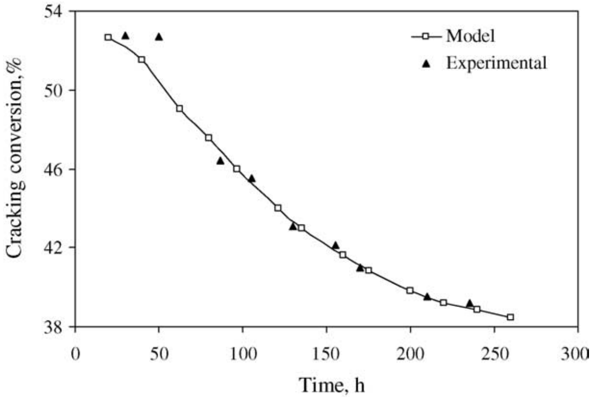

Fig. 18. Conversion of >370 °C feed with time on stream (CoMo/Al_2O_3; 3 MPa; 723 K) [69].

closely predict the catalyst life. Figs. 19 and 20 are another illustration of how a model can closely predict catalyst life. These results were obtained by de Jong et al. [69–71] during hydroprocessing of a Kuwait vacuum gas oil over CoMo/Al_2O_3 catalyst at 3 MPa. It is evident that both the effect temperature on coke deposition as well as the gradual decline in hydrocracking activity could be predicted by model. Moreover, the model predicted an unusual maximum in coke formation due to the increased transfer from the liquid to gas phase operation with increasing temperature. The same was confirmed experimentally.

3.6. Matching catalysts with reactors and feeds

Several types of reactor systems suitable for hydroprocessing of heavy feeds were developed and commercialized. In every case, the aim was to extend the operation by avoiding frequent catalyst replacements. The matching of catalyst properties with type of reactor for achieving an optimal operation is much more complex for heavy feeds than that for light feeds. This was indicated by detailed discussions published elsewhere [42,72]. Therefore, only a brief account of these issues will be given.

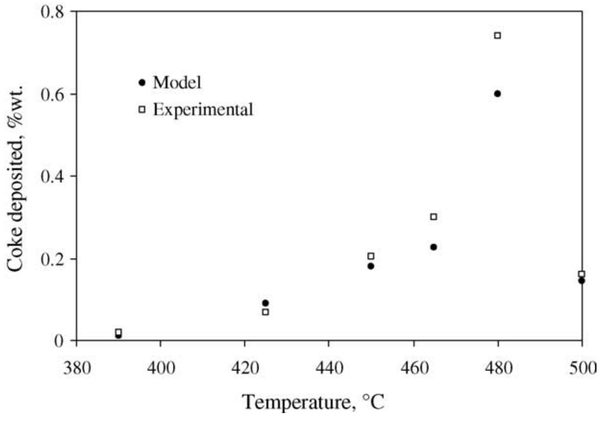

Fig. 19. Effect of temperature on coke formation (>370 °C feed; CoMo/Al_2O_3; 3 MPa) [70].

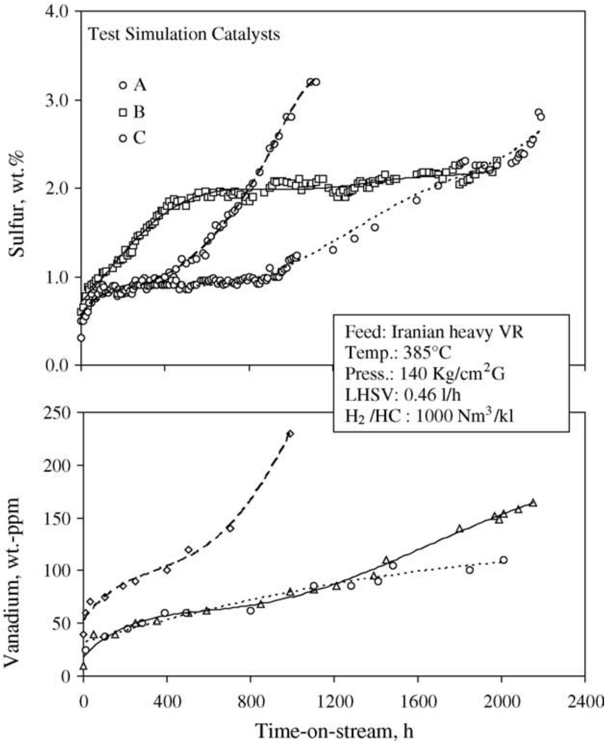

Fig. 20. Simulation for catalyst aging test [71].

The content of metals in the feed is one of the parameters used for selecting the type of catalytic reactor. It was suggested that the feeds containing less than 100 ppm of metals can be processed using a fixed bed reactor. For feeds containing between 25 and 50 ppm, a dual catalyst system may be required, i.e., the front-end should possess a high metal tolerance, whereas the tail-end a high catalytic activity. For metal contents ranging between 50 and 100 ppm, a triple catalyst system with the front-end HDM catalyst having a high metal storage capacity guard reactor, may be required. When metal content approaches 350 ppm, two guard reactors may be necessary [73]. There is a limit on the size of catalyst particles allowing a smooth operation of fixed beds without causing significant pressure drops forcing shut-downs of the operation. To a certain extent, this problem was overcame by the development of fixed beds allowing periodic catalyst replacements during the operation, e.g., the quick catalyst replacement reactor developed by Shell [59], on stream replacement reactor developed by Chevron [74], etc.

Ebullated bed reactors allow a periodic addition and withdrawal of catalyst without interrupting the operation. In this case, there are no problems with the pressure drops which are encountered in fixed bed reactors. Therefore, the size of catalyst particles less than 1 mm can be used without any difficulties. The flexibility of the ebullated bed reactors, enabling hydroprocessing of the wide range of heavy feeds should be noted. Moreover, depending on the refinery strategy, the reactors can be operated either in a low conversion mode or a high conversion mode.

The best known moving bed reactor is the ‘‘bunker reactor’’ [75]. This reactor combines the advantages of fixed bed operation in a plug flow and ebullated bed reactor enabling easy catalyst replacement. The trickle-flow system employed allows a discontinuous catalyst replacement without interrupting the operation.

3.7. Regeneration of catalysts

The regeneration usually involves the burn-off of coke deposited on the surface of spent catalysts [37]. To avoid temperature run-away, the burn-off has to be carried out in a diluted air. Table 5 shows the properties of NiMo/Al_2O_3 catalyst used in two different HDM operations, i.e., catalyst A contained about 6 wt.% of V + Ni, whereas catalyst B almost 25% of V + Ni + Fe [76]. It is evident that a large portion of the original surface area could be recovered. In spite of this, the activity recovery was rather low because of the detrimental effect of metals. Burn-off in air resulted in a significant sintering of catalysts due to the uncontrolled temperature run-away. Table 5 clearly indicates that the presence of metals, which deposited on catalyst surface during hydroprocessing of heavy feeds complicates catalyst regeneration for reuse. At the same time, for catalysts used for hydroprocessing of the metals free feeds, a similar burn-off may be sufficient for recovering more than 80% of the original activity [37].

In a multi-reactors system, most of the metals are removed in the first reactor using a macro-porous catalyst. This diminishes catalyst deactivation in the down stream reactors. For example, the ARD process employs total of four fixed bed reactors in a series. It is then obvious that the catalyst regenerability will increase from the first reactor towards the last reactor. In the case of processes employing fixed bed reactors, acceptable performance can only be achieved using feeds containing less than 100 ppm of metals total. This suggests that catalysts, e.g., those from the last two reactors of the ARD process, may be regenerated for reuse. Ebullated bed reactors are used for hydroprocessing of heavy feeds containing more than 100 ppm of metals. In this case, only a small portion of the original activity may be recovered. Therefore, regeneration of spent catalysts may not be justified. Safe methods for handling, disposal and transportation of these catalysts have to be identified. In some cases, the metal reclamation is an attractive option. Some heavy feeds contain more than 1000 ppm of metals. For such feeds, a carbon rejecting option (e.g., coking) may be more advantageous than catalytic hydroprocessing.

Table 5
Properties of fresh and regenerated catalysts [77]

Catalyst	Treatment	SSA (m^2/g)	Conversion (%)	
			HDS	HYD
Fresh	None	140	46.7	27.5
Spent A	None	17	–	–
Spent B	None	11	–	–
Spent A	2% O_2	127	15.0	10.7
Spent B	2% O_2	60	15.7	12.9
Spent A	Air	54	12.3	9.3
Spent B	Air	17	6.4	5.0

SSA: specific surface area.

During hydroprocessing, most of the V deposits on the external surface of catalyst particles, whereas Ni is more evenly distributed. Consequently, V has more detrimental effect on activity than Ni. The presence of V on the external surface of catalyst particles provides an opportunity for its V removal by leaching. These methods, termed as rejuvenation, have been evaluated by several authors [16,76]. Thus, Marafi et al. [77] used aqueous solutions of organic acids such as oxalic acid, citric acid, tartaric acid and malonic alone or in a solution with $Al(NO_3)_3$. About 70% of the original activity could be recovered by leaching a spent catalyst with these solutions. Inorganic solutions containing H_2SO_4, HCl and Fe^{3+} were also investigated [78,79]. Similarly as for the organic agents, about 70% of the original HDS and HDN activity could be recovered. It is noted that aqueous solutions treatments may affect mechanical properties of catalyst particles.

4. Future prospectives

Significant advances have been made in the understanding of the role of conventional catalysts during hydroprocessing. The effects of additives such as fluoride, phosphate, borate and others were clarified to the point that some of them are already being added to commercial catalysts. Their beneficial effect results from slowing down deactivation and thus prolonging catalyst life. Catalyst functionalities can be further modified by supports. Supports which are more acidic than γ-Al_2O_3 improve hydrocracking activity, but they also may increase the rate of coke formation. With respect to heavy feeds, additional research is needed to design a catalyst with desirable hydrocracking activity and at the same time be resistant to deactivation. Several studies have shown that further improvement in catalyst activity can be realized by modifying the method of preparation and pretreatment. The H_2S/H_2 ratio has emerged as an important parameter for maintaining a high catalyst activity and/or for extending catalyst life. Most of the studies involved model compounds mixtures and light feeds containing neither metals nor asphaltenes. Benefits of the new information from these studies have not been fully utilized and applied to catalysts used for hydroprocessing of heavy feeds. It is believed that during hydroprocessing of heavy feeds, catalyst life can be further prolonged by applying new knowledge.

Among non-conventional catalysts, metal carbides and nitrides have been tested for hydroprocessing. However, rather peculiar trends in their intrinsic activity make them unsuitable for hydroprocessing. Noble metal sulfides based catalysts are known for exhibiting very high HYD activity, whereas their activity for hydrocracking and hydrogenolysis are rather low. This may be overcome by combining noble metal sulfides with acidic supports such as zeolites. After being used in hydroprocessing of heavy feeds, the recovery of noble metals from spent catalysts is believed to be difficult and costly. Therefore, their potential of being used in similar applications is rather low. It has been noted that high conversions were achieved when fine catalyst particles were slurried/dispersed in a heavy feed. With respect to catalysts, this may be a ‘‘once through’’ option. Thus, it may not be possible to recover catalyst for reuse. Low cost, throw-away materials possessing catalytic activity may be identified. In this case, the ''once through'' option may be more attractive.

The properties of heavy feeds, particularly content of metals and asphaltenes should be established above which hydroprocessing becomes less attractive than a carbon rejection methods. Thus, coking of high metals and asphaltenes heavy feeds such as residues derived from heavy crudes may have more merit, particularly if it is integrated with an efficient utilization of petroleum coke. For example, commercially established routes involve production of electricity. Furthermore, low cost petroleum coke may be gasified to synthesis gas which in turn can be used to produce sulfur free liquid fuels via Fischer–Tropsch synthesis. In this case, a low value material is converted to a high value fuel. The costs associated with the deep-HDS or even ultra deep-HDS suggest that this method for production of liquid fuels should be reexamined and compared with the cost of fuel products produced by conventional methods.

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