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Towards improvement of hydroprocessing catalysts - understanding the role of advanced mineral materials in hydroprocessing catalysts

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Abstract

Mineral materials play a pivotal in heterogeneous catalysts as active, support, or promoter components, with the oil refinery industry being one of the biggest beneficiaries. While conventional hydroprocessing catalysts have historically met the industry's needs, the growing need to accommodate unique feedstocks, meet the increasing demand for environmentally acceptable products, obtain better product specifications, enhance selectivity for reactions to increase ratios for certain product cuts, and use more cost-effective and abundant mineral materials, has recently motivated for fresh considerations in the development of hydroprocessing catalysts. Based on periodic trends, noble metals possess the most desirable qualities, but their relative abundance in the Earth's crust is too low to meet industry needs. They are costly and highly sensitive to sulfur poisoning. Mo and W lie in the sweet spot, but it is anticipated that they cannot meet the increasing demand. Investigations of electronic interactions of more economical and abundant metals, such as Nb, V, and Fe, with other elements and support materials have yielded a better understanding of synergistic effects that help to access noble metal-like qualities. This work contrasts conventional hydroprocessing catalysts and recently improved catalysts, detailing the chemistry considerations behind the selection of mineral materials used in the catalysts. It also explores how further manipulation of these mineral materials and synthesis approaches is driving toward more desirable properties. The work brings to the attention of the readers the challenges and opportunities for the further improvement of hydroprocessing catalysts to ensure environmental sustainability while meeting the industry's growing needs.

Keywords: Hydroprocessing, hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation, hydrodemetallization and hydrocracking



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INTRODUCTION

The ability of humans to interact with their environment was greatly enhanced with the advent of exploiting mineral materials in our ecosystem during the stone, bronze, and iron ages, defining key functional points of the earliest evident civilizations based on the abilities to modify and add certain characteristics to these materials through various treatments. Human reliance on mineral materials continues, with most modern advancements, manufacturing, and processing relying on mineral material catalysts. The hydroprocessing industry is one such prominent industry where different kinds of catalysts are required at numerous stages to access various products^[1,2]. The growth of the petroleum refinery is attributed to be the biggest driver of the growth of the global catalyst market, which is expected to grow to USD 9.5 billion by 2027^[2]. These catalysts are mostly different combinations of transition metal silicates, phosphates, carbonates, sulfates, sulfides, nitrides, carbides, phosphides, borides, oxides, and hydrides, with various other elements such as phosphorous, boron, and fluorine being added to improve catalyst properties. Mineral materials, such as alumina, zeolites, titania, cerium, and zirconia, are also crucial as catalyst support materials^[3]. Research for improving catalysts for these processes remains a prominent and active area of study^[1]. Improved catalysts can reduce refinery costs, improve selectivity for certain products, allow non-conventional feedstock, such as creosotes, to be accommodated, and make them economically attractive fuel sources^[4].

While the relative abundance of mineral materials used for current hydroprocessing catalysts is generally not a problem, the increasing demand for petroleum products and the need for more active and highly selective catalysts to improve refinery processes will change this situation. There is also a tendency to incline towards the noble metals, which have demonstrated superiority among all active elements. Research seeks to bridge the gap by manipulating properties of more abundant elements (e.g., iron) to achieve the same level of efficiency to ensure sustainability^[5]. The pursuit of improvements in this field is broad, including changes in support materials, improved synthesis protocols, and the incorporation of multifaceted compositions that result in better catalyst properties. On the same note, the importance of recycling spent catalyst materials and the environmental concerns associated with the discarding of the modified mineral materials must also be stressed enough^[6]. Sufficient studies are also required to understand the impact of modified mineral materials used in hydroprocessing catalysts on the environment.

Performances of conventional hydroprocessing catalysts used in typical hydroprocessing reactions are discussed, articulating the roles played by the various constituents of the catalysts that are obtained from a wide array of typical mineral materials. Chemistry aspects that motivated the combinations of choice mineral materials used in the conventional hydroprocessing catalysts are discussed. Their limitations (e.g., poor activity for some reactions, poor product selectivity, and catalyst deactivation) are also discussed, and we proffer solutions through this review work. The superiority of noble metals is identified throughout all the discussions, emphasizing the aim to manipulate combinations of more affordable and abundant mineral materials to achieve similar desirable properties. The current position in the development of catalysts to overcome challenges associated with the growing need to accommodate hydroprocessing of unconventional feedstocks, such as creosotes and bio-oils, with examples of promising catalysts, is also well covered.

HYDROPROCESSING IN GENERAL

Hydroprocessing reactions

Hydroprocessing reactions seek to modify the hydrocarbon composition to achieve desirable fuel specifications and eliminate heteroatoms to protect the environment and downstream processes^[3,7]. Reactions such as the addition of hydrogen to carbon-carbon double bonds (hydrogenation), breaking of

C-C bonds (hydrocracking), hydroisomerization, reforming, and polymerization are required to upgrade feedstocks, such as heavy oils and oil residues, to meet fuel specifications, including lower boiling points^[8]. Heteroatom elimination reactions are known as catalytic hydrotreating reactions, include removal of sulfur, nitrogen, oxygen, and metal, and are referred to as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO), and hydrodemetallization (HDM), respectively^[9]. HDS and HDN reaction mechanisms [Figure 1] are representative of the reaction mechanisms behind hydroprocessing reactions.

Hydroprocessing reaction competitions

Hydroprocessing reactions occur simultaneously, competing with each other, usually causing a retarding effect on each other^[4,10]. Equilibrium constants for the competition of catalyst sites by the heterocyclics generally increase in the order of aromatic hydrocarbons < sulfur compounds < oxygen compounds < nitrogen compounds. HDN is generally more difficult compared to other hydroprocessing reactions that occur simultaneously, with an inhibitory competitive effect, and can be used to dictate the hydrotreating operating conditions^[11-14]. For example, high N content (> 60 ppm) negatively affects the ability to achieve deep HDS (less than 10 ppm wt. S)^[13,15]. The competitive behavior in the adsorption of heterocyclic compounds on the active sites of hydroprocessing catalysts results in differences in selectivities and reaction depths of the catalysts^[15-18]. Different sites for cleavage of C-S, C-O, C-N, and other reactions are also proposed^[11]. The need to establish the different sites associated with specific reaction selectivities has created several research questions that have aided the conceptualization of various strategies for improving the catalysts based on composition or design for specific or multiple reactions^[11]. Catalyst stacking technologies are also being used to maximize the complementary participation of different catalysts and their different active sites to obtain high performances for multiple reactions^[19]. Improved catalysts can reduce the cost of refining crude oil, especially creosotes and other synfuels, making them economically attractive fuel sources^[4].

Traditional hydroprocessing catalysts

Hydroprocessing catalysts are usually made up of different combinations of active metals, promoter metals, support materials, and other additives that help improve catalyst properties. Catalyst activity increases with an increasing percentage of active metals up to a certain point where the activity will start decreasing. As such, there is a need to balance between the increasing cost of catalysts as the percentage of active metal increases and the benefits of obtainable catalyst activity^[11,20]. Transition metal sulfides are the most prominent materials in hydroprocessing catalysis^[21]. The traditional catalysts for hydrotreating are the sulfided combinations of alumina-supported Mo or W promoted by Co or Ni; CoMo/Al₂O₃, NiMo/Al₂O₃, and Ni(Mo)W/Al₂O₃ being the most common commercial examples^[19,22]. They are considered the baseline catalysts for benchmarking the performance of potential catalysts. Environmental concerns and the need to accommodate harsher feedstock and shape products have been the main drivers for the continuous development of hydroprocessing catalysts^[19,23,24]. These subjects are discussed in greater depth in our previous review^[25].

Periodic trends of metals in hydroprocessing

Electronic properties of the selected metals used in the catalysts lay the foundations for understanding catalyst activity and selectivity. Pecoraro and Chianelli^[26-29] carried out transition metal tests on HDS activity [Figure 2A], while Eijsbouts^[26-29] carried out similar tests on HDN [Figure 2B]. All the studies confirmed that the primary effect for activity is electronic and is related to the position the metals occupy in the periodic table. For both processes, transition metals occupying the first row in the periodic table are relatively inactive, while those occupying the second and third rows have high activity. HDS conversion levels are high for Ru, Os, Ir, Rh, and Re, respectively, while HDN conversion levels are high for Ir, Os, Re,

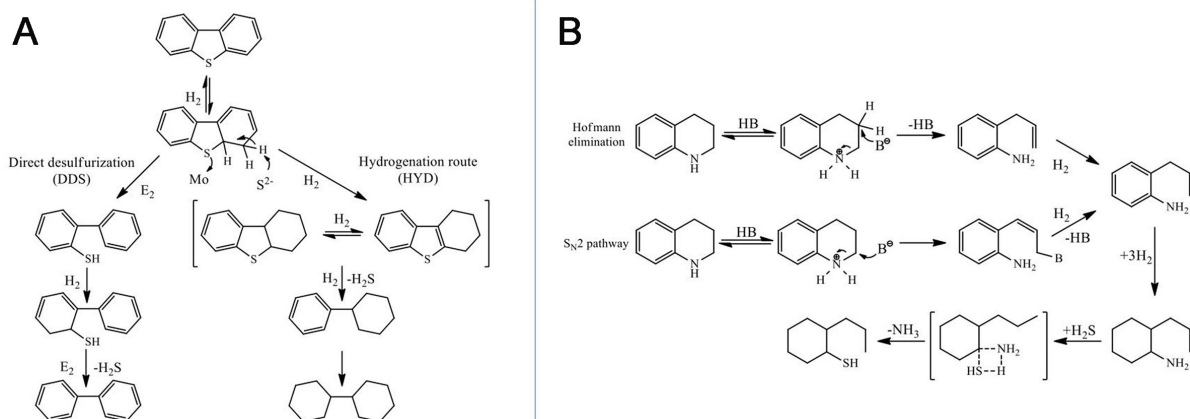


Figure 1. Schematics showing (A) HDS and (B) HDN reactions of typical sulfur and nitrogen containing compounds as representative hydroprocessing reactions. DDS: Direct desulfurization; HDN: hydrodenitrogenation; HDS: hydrodesulfurization; HYD: hydrogenation.

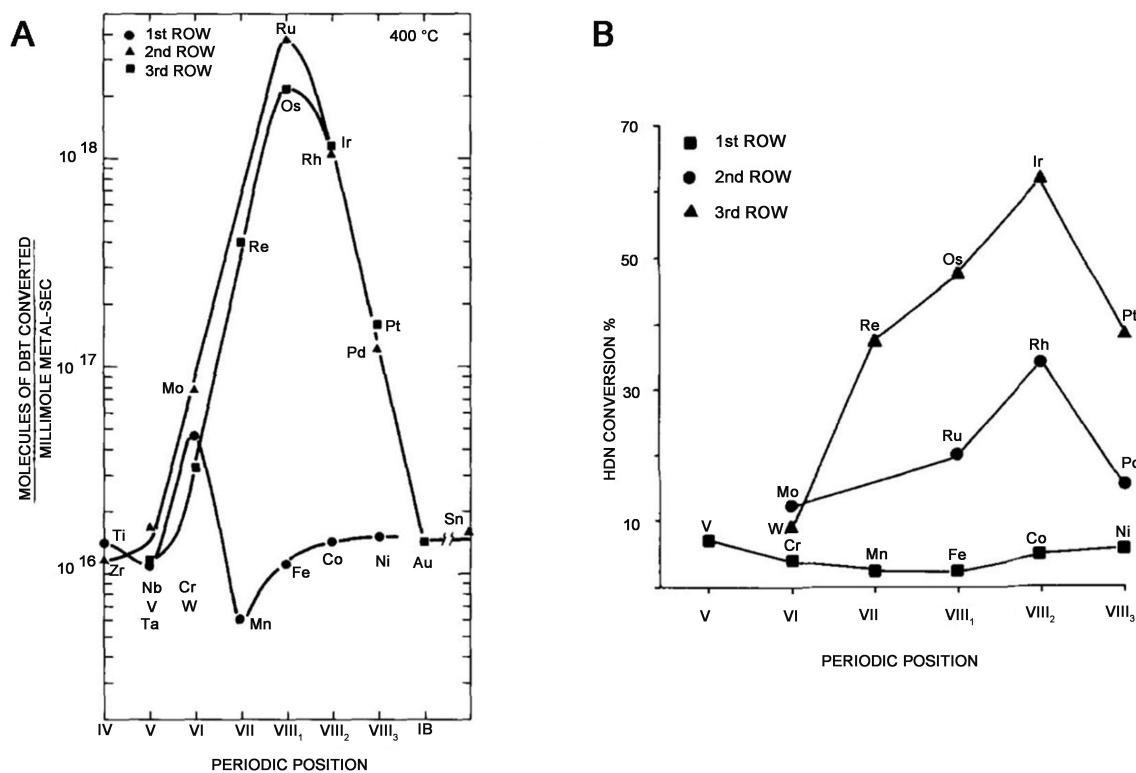


Figure 2. Periodic trends for (A) conversion of dibenzothiophene; (B) conversion of quinoline. Reprinted from references [26-28,31] and [26-28,31] with permission from Elsevier.

Pt, and Rh, respectively. The HDN maxima were found to be at V, Rh, and Ir for the first-row, second-row, and third-row elements, respectively^[29]. First-row carbon-supported transition metal sulfides had low quinoline conversions with a minimum at Mn/C and Fe/C and maxima at V/C and Ni/C, while the second- and third-row transition metal sulfides had their minimum with Mo/C and W/C, and the maxima at Rh/C and Ir/C. Noble metal catalysts (Rh/C, Pd/C, Os/C, Ir/C, and Pt/C) show the highest activities and selectivity for propylcyclohexane in quinoline HDN^[28]. Raje *et al.* also reported similar volcano plots when they tested second-row unsupported transition metal sulfides: Zr, Nb, Mo, Ru, Rh, and Pd sulfides in the

HDS, HDN, and HDO of coal-derived naphtha that contained significant amounts of S-, N-, and O-containing compounds^[30]. Reactivities followed the order: Ru > Rh > Mo > Pd > Zr > Nb, and RuS₂ emerged as the best catalyst for all the processes. Selectivities for hydrogenation vs. hydrogenolysis have also been mapped, highlighting the importance of the position of the metals on the periodic table^[31]. Observations are that W, Pt, Ir, and Ru are highly selective for hydrogenation.

Understanding periodic trends has motivated the manipulation of electronic properties of various active phases through the use of additives (halogens and phosphorus), chelating ligands, and promoters to facilitate catalyst preparation or performance, usually targeting the use of more affordable metals to obtain noble metal-like characteristics^[20].

ROLES OF MINERAL MATERIALS AS SUPPORT MATERIALS IN HYDROPROCESSING CATALYSTS

Catalytic supports play a crucial role in dispersing deposited metals, increasing surface stabilization against deactivation processes such as agglomeration, improving the morphology of the active sulfide component^[32], providing beneficial characteristics towards reactions such as defect sites, and enhancing the charge transfer ability and hydrogen spillover^[33]. Catalyst supports can also provide additional functional sites and stabilize catalyst active sites. A new active phase on the surface of the catalyst may be formed via the interaction of the support with the catalyst. The following characteristics need to be considered when choosing hydroprocessing support materials: mechanical and thermal stability, surface area, acidity, and porosity^[34,35]. The composition and distribution of Brønsted acid and Lewis acid sites are also important^[36,37]. Brønsted acid sites are important for promoting the dispersion of the active metal, reducing the reduction temperature of the active metal, and modulating the interaction between the support and the metals. Lewis acid sites are regarded as adsorption sites of the heteroatomic compounds, and they play a role in selectivity *via* hydrogen spillover effects. Supports function differently depending on the strength of their acid sites, and optimal acidity is required for the activity and selectivity of reactions^[38]. Metal oxides, such as Al₂O₃, SiO₂, ZrO₂, TiO₂, and CeO₂, and carbon materials have been investigated as hydroprocessing catalyst supports^[32,35,39].

Support materials form the basis of hydrocracking reactions with the Brønsted acid sites and play a crucial role in the activity and selectivities of the catalysts^[40]. Co-Mo/MCM-41 showed a high yield to the skeletal isomerization reactions because of its strong surface Brønsted acidity and relatively low hydrogenation activity compared to Ni-Mo/MCM-41 and Co-Mo/c-Al₂O₃, which exhibited the low selectivity to the isomerization reactions owing to their high hydrogenation activities^[41]. [Table 1](#) summarizes the properties of typical support materials that have been used in hydroprocessing catalysts.

Alumina supports

Alumina supports are the most widely used in industrial applications since they are inexpensive and readily available, with good chemical and thermal stability and excellent surface area. However, the main challenge is its strong interactions with the active metals, which negatively affects catalytic activity^[51,52]. During the synthesis of the catalysts, the impregnated metal precursors, Co/Ni(Mo/W), interact with the support, and the high affinity of Ni²⁺/Co²⁺ ions coordinating with the Al³⁺ surface vacancies can lead to the formation of strongly bonded spinel-like NiAl₂O₄ structures, resulting in low catalytic activity due to limited availability of Ni ions to form the active phases Co(Ni)Mo(W)S^[52]. Mo₂C, MoS₂, PtO₂, Pt/C, Pd/C, Ru/C, and Rh/C, sulfided Pt/C and sulfided Pt/γ-Al₂O₃ were compared in the HDN of pyridine, and Pt/γ-Al₂O₃ was the most active^[53]. The catalysts followed the trend: Pt/C > Pd/Al₂O₃ > Pd/C > Ni₂P > Pt₂₀Ru₁₀/C > Pt/Al₂O₃ in the conversion of pyridine^[54]. HDO activity using Pt was influenced by the type of support used, showing the

Table 1. Typical hydrotreating supports

Support	Synthesis methods	Mass composition	Surface area (m ² ·g ⁻¹)	Acidity composition (@200 °C)		Comments	Ref.
				LASs	BASs		
SBA-16 and Al-Ti-SBA-16	Two-step method	Al ₂ O ₃ (0%-10%) and TiO ₂ (10%)	975.7 and 969.6	21.4 and 83.7	21.9 and 26.7	Highly ordered structure and enhancing acidity.	[42]
TiO ₂ -Al ₂ O ₃ (Ti/Al 0-4)	Pre-hydrolysis co-precipitation method	Ti/Al -0, 0.96, 1.93, 3.88	250.8	Weak acid sites (-65.3), moderate acid sites (-58.5), and strong acid sites (-12.4)	-	Ti modification can modulate metal support interaction, Al-O-Ti bonds formed, and reduced acid sites. Ti enhanced HYD and CUS.	[34]
TiO ₂ -Al ₂ O ₃	Solvent evaporation-induced self-assembly method	Ti -0, 10, 20, 40%	428, 391, 365, 296	Weak acid sites (μmol·g ⁻¹) (-196) and strong acid sites (-68)	-	20% support increase of TiO ₂ increased pore size, decreased strong acid sites.	[43]
TiO ₂ -Al ₂ O ₃	EISA method	Ti/Al 0, 0.2, 0.4, 0.6	241, 273, 284, 207	Weak acid sites (mmol·g ⁻¹) -0.082 Medium and strong acid sites -0.022	-	Highly ordered structure with high surface area, narrow pore size distribution, and high stability, Ti-O-Al bonds formed, Ti and Al homogeneously distributed.	[44]
-γ-Al ₂ O ₃ -HZSM-5 -γ-Al ₂ O ₃ -MCM-41	Physically blending method	HZSM-5 (5%, 10%, 20%), MCM-41 (5%, 10%, 15%)	215	0.33 (μmol·m ⁻²)	0.49 (μmol·m ⁻²)	Higher surface area, increased BAS/LAS obtained.	[45]
C@γ-Al ₂ O ₃	Chemical vapor deposition	-	259, 249, 207	Total acidity 315 (μmol·g ⁻¹)	-	Higher dispersion of the active metal and promotion of MoS ₂ by Co.	[46]
NPC@γ-Al ₂ O ₃	Pyrolysis of phytic acid and urea impregnated on γ-Al ₂ O ₃	0.7 g of phytic acid, 0.7 g of urea	220	57 (μmol·g ⁻¹)	0.48 (μmol·g ⁻¹)	High electron donating effect of N and P; decreased acid sites on the support.	[47]
Zeolite-activated carbon (ZAC50%)	Reflux	50wt.% activated carbon	379	-	-	Uniform mesoporous structure, moderate acidity, and better active metal dispersion.	[48]
SBA-15, activated carbon, mesoporous alumina	So-gel, commercial activated carbon	-	573, 447, 276	-	-	SBA-16, AC showed a high surface area; the mesoporous catalyst showed higher hydroprocessing and hydrocracking activity due to higher pore size and dispersion.	[49]
Hexagonal mesoporous silica [Ti-HMS (Si/Ti 20, 40, 60)]	Post-synthesis method	-	285	-	-	Ti-incorporation improved the catalytic activity, and Ti-HMS (Si/Al 20) showed more dispersion of the active phase.	[50]
Pseudoboehmite	Eco-friendly technology (reprecipitation) and hydrothermal treatment	-	192	-	-	Bimodal pore distribution. Catalyst supported on H1 has more CoMoS phase.	[35]
Mesostructured titania	-	-	-	-	-	Higher specific surface area.	[51]
Al ₂ O ₃ -CeO ₂	Sol-gel	CeO ₂ loadings (0wt.%, 5wt.%, 10wt.%, and 15wt.%)	-	-	-	15wt.% CeO ₂ loading resulted in 97% DBT HDS conversion and inhibited the formation of NiAl ₂ O ₄ spinel and increased BAS.	[52]

BASs: Brønsted acid sites; EISA: facile evaporation-induced self-assembly; LASs: Lewis acid sites.

trend: Pt/Al₂O₃ > Pt/ASA > Pt/TiO₂ > Pt/CeZrO₂ > Pt/ZrO₂ > Pt/CeO₂^[55]. However, coke formation was cited as the biggest challenge with these catalysts^[56]. While the traditional alumina-supported catalysts do well for HDO, alumina is unstable in the presence of high levels of water and is highly vulnerable to coking due to the acidic sites^[24].

Mesoporous silica supports

Mesoporous silicas have excellent physicochemical properties, such as high surface area, large pore size, and structural order^[39,42,57]. Silicas provide moderate metal-support interaction and well-dispersed active metals, resulting in good catalyst performance^[58]. The textural properties of SBA-15 are desirable for HDS of refractory sulfur compounds, including stability under harsh hydrotreatment conditions^[57]. Liu *et al.* investigated NiMo catalysts supported on SBA-15 and -Al₂O₃ for the HDS of 4,6-DMDBT and found good dispersion of active metals and high HDS activity compared to -Al₂O₃-supported catalysts^[58]. SBA-16 promoted good dispersion of active metals and is reported to be good for hydrogenation catalysts with large pores that promote mass transfer^[42]. Hydrocracking properties of Pd (1%) loaded mesoporous silicas (MCM-41, MCM-48, SBA-15 ASA) were investigated, and a cracked product distribution was found to decrease with loss of mesopores while low metal dispersion resulted in overcracking due to long poor residence time of olefins^[59]. However, the low acidity of mesoporous silicas limits their range of application as catalytic supports^[57].

Titania, zirconia and ceria supports

Titanium dioxide has been widely used in hydroprocessing catalysts and is reported to promote better dispersion (e.g., of MoS₂) and increased acidity^[36,56]. However, conventional TiO₂ has not penetrated commercial applications as much as alumina because it suffers low mechanical strength and specific surface area^[51,60]. Several strategies have been developed to obtain TiO₂ with better pore sizes and specific surface area, but crystallization during preparation leads to the collapse of the porosity^[46]. Better HDS reactivity by weakening the geometric constraint through dealkylation and/or isomerization has been reported through TiO₂ and ZrO₂^[61]. TiO₂ and ZrO₂ have been reported to be ideal as HDO catalysts. Sudhakar *et al.* found that these supports provide additional HDO sites, stabilize the catalyst active sites, and enhance resistance to coking^[22]. Cerium dioxide (CeO₂) is one of the most abundant rare earth metals and has attracted attention due to its properties such as chemical stability. It shares many similar properties with TiO₂^[62]. CeO₂ has good chemical stability, can play a role as a promoter, can activate H₂, and promotes the effective dispersion of the active metal. Rare earth metals generally have less carbon deposition, and CeO₂ has a lower tendency for coke formation^[63,64]. It is particularly valuable for HDO due to its ability to generate oxygen vacancies and activate H₂ and C=O bonds^[56]. However, it is worth noting that CeO₂ is relatively expensive and has low surface area and poor thermal and mechanical properties^[39]. Good acidity for C=O bond activation has been reported in TiO₂, ZrO₂, and CeO₂, and the order of their acidity follows the order TiO₂ > ZrO₂ > CeO₂^[56]. Small surface area, lack of porosity, and deactivation at high temperatures have been cited as challenges in these metal oxides, encouraging the use of aluminosilicates^[56].

Zeolite supports

Hydrated aluminosilicates (zeolites), such as NaY, SAPO-11(34), USY, and ZSM, are gaining more attention as supports due to their good balance of Bronsted and Lewis acid sites, good crystalline structure and controlled porosity, high thermal and mechanical resistance, ease of dispersing active phases optimally, and large surface area^[65]. Much attention towards them has increased due to their high isomerization and cracking activities^[34,66]. They play an important role in the morphology of the active phase^[66]. Y-zeolites are more dominant in commercial hydrocracking applications, while ZSM-5-type materials are preferred for hydrodewaxing or shape-selective cracking^[67]. Zeolite desilication was found to improve the performance of a PtPd/HY catalyst in the hydrocracking of a plastic pyrolysis oil/vacuum gas oil blend^[68]. Drawbacks with

zeolites include limited pore accessibility and distribution, diffusion barriers, and deactivation by coking^[65,69]. Sometimes, strong Bronsted acid sites in zeolites lead to unwanted over-cracking of hydrocarbons and carbon deposition. To mitigate these challenges, various metals, such as Ni, Pt, Rh, Re, La, Bi, Mg, K, and Mg non-metals, such as P and B, have been incorporated in the support^[43,66,70-74]. Ga was found to be the most suitable^[43,61,75]. Zhou *et al.* demonstrated that Ga weakens the acid site strength on the surface of Y zeolites by acting as a weak electron acceptor compared to Al^[66]. Zeolites have also been successfully employed in HDO but also show dealumination and high coke formation^[76]. A high acidity and well-balanced ratio of micro- and meso-porosity was found at a higher SiO₂/Al₂O₃ ratio, giving high activity in a Ni-W/Zeolite-Y catalyst^[77].

Carbon material supports

Carbon materials show good thermal conductivity, textural and structural characteristics, weak interaction with active metals, higher dispersion of active metals, higher resistance to coke deposition due to the absence of acidity, lower tendency of nitrogen poisoning, wide transport pores that limit the formation of condensation products during hydrotreating reactions, and good electron transport capability^[46,78,79]. However, it is important to note that different types of carbon materials have different characteristics. Pure carbon materials and activated carbon materials have poor mechanical properties, low density, and microporosity, while mesoporous carbon material is known to have a low surface area, low mechanical strength, and bulk density^[46]. Multi-walled carbon nanotubes (MWCNTs) have high surface area, high pore volume, relatively high mesopore diameter, and almost complete absence of micropores. MWCNT-supported catalysts were credited to having a low crystallinity that increases the ability to adsorb hydrogen and act as a hydrogen transfer agent during the hydrogen spillover from the active sites to the adsorbed feedstock molecules, resulting in increased HDS and hydrogenation (HYD) activity and reduced N-containing compound inhibition^[32]. Carbon-supported catalysts have lower HDO activity for carbonyl, carboxyl, and methoxyl groups compared to alumina-supported catalysts^[24].

Improved support materials

Various strategies have been used to improve support materials and enhance the performance of hydroprocessing catalysts^[32]. Changing the support preparation method, use of novel precursors, additives, and chelating agents, blending different support materials, and other modification methods have been used to overcome challenges such as strong metal-support interactions^[80]. Various support materials have been mixed together to explore the combination of positive characteristics from these individual materials and overcome their drawbacks. These combinations include TiO₂-Al₂O₃, Al₂O₃-SiO₂, TiO₂-ZrO₂, TiO₂-SiO₂, MCM-41-Al₂O₃, USY, ZSM-5, Ti-SBA-15, MCM-41, Ti-HMS, TiO₂-MgO, Al₂O₃-MgO, CeO₂-Al₂O₃, Al-SBA-15, Al-SBA-16, SiO₂-ZrO₂, SiO₂-TiO₂, Al₂O₃-B₂O₃, and SiO₂-MgO. Additionally, composite materials have been developed, including alumina-carbon, alumina-carbon nanofiber alumina-graphene, alumina-carbon nanotube, zeolite-carbon, and zeolite-carbon nanofiber^[32,35,48,58,60,63,80-83].

Silica-alumina-supported NiMo, CoMo, and NiW catalysts show higher HDN, hydrocracking, and hydrodearomatization activities compared to alumina^[84]. Much higher hydrocracking activity has been reported through amorphous oxide supports such as amorphous silica-alumina compared to crystalline supports such as zeolites^[67]. Reducible metal oxides (TiO₂, CeO₂) have been used as electronic and structural promoters to improve the catalytic activity, selectivity, and thermal stability of the catalysts^[63]. Incorporation of Ti can improve the dispersion of the active metals; it can donate electrons to the conductive band of the active metal, weakening the metal-oxide interaction and making it easier to sulfide, and also weakens the metal-sulfur bond energy forming more coordinatively unsaturated sites (CUS) that increase catalytic activity^[42,85,86]. The incorporation of Al and Ti in mesoporous silica SBA-15 improves the acidity on the surface^[57]. Increasing Si/Al molar ratios (up to 20) in Al-modified SB-15 supported NiMo catalyst resulted

in increasing 4,6-DMDBT HDS activity owing to good dispersion of active metals^[36,42,87]. TiO₂-Al₂O₃ has superior HDN catalytic performance due to excellent hydrogen transfer capacity and suitable acid properties^[51,88]. Better dispersion of CoMoS was obtained on a TiO₂-SBA-15 composite, resulting in higher DBT and 4,6-DMDBT selectivity and conversion^[51]. Ceria has been incorporated into alumina to produce a material with a higher surface area, increased thermal resistance, reduced carbon deposition, improved dispersion of metals on the surface, and better interaction between the active metal and the support^[64]. CeO₂ promotes the HDN activity of Ni₂P^[64]. Xia *et al.* conducted a study on CoMo/ γ -Al₂O₃ catalysts modified with Ce, and they concluded that the introduction of Ce adjusted the acidity properties of the support, formed new BAS and increased the BAS/LAS ratio, resulting in excellent isomerization performance^[85]. A carbon/zeolite composite with attractive properties from both materials was reported^[38]. The addition of halides (especially F and Cl), P, and B to support materials has also been reported, usually to improve support acidity^[9,89]. Promotional attributes are also given to these additives, with improved HDS and HDN activity in conventional catalysts and enhanced hydrogenolysis and cracking in hydrocracking catalysts^[90]. Rare earth elements (La, Ce, Nd, and Pr) have been used to modify the acidity of Y zeolites (SiO₂/Al₂O₃ \approx 25)^[89].

Considerations for catalyst preparation methods and the nature of the precursor components also need to be made. He *et al.* employed three different synthesis methods (impregnation, co-precipitation, and sol-gel methods) to obtain TiO₂-Al₂O₃ binary oxide composites and found that the catalyst synthesized using the co-impregnation method possessed the highest specific surface area, while the one by the sol-gel method showed higher pore volume and better mesopore distribution^[86]. Yan *et al.* demonstrated through NiW-HY + Al₂O₃ and by NiW-Al₂O₃ + HY that the order of metal support combination methods played a crucial role in the performance of catalyst performance when they observed significantly different activities and selectivities^[91].

ROLES OF MINERAL MATERIALS AS ACTIVE METALS AND PROMOTERS IN HYDROPROCESSING CATALYSTS

Active and promoter mineral materials in hydrodesulfurization catalysts

Conventional hydrodesulfurization catalysts

Conventional HDS catalysts are obtained through sulfidation of metal oxide precursors, i.e., Mo or W oxides (active metal) promoted by Co and/or Ni supported on a support such as Al₂O₃ and TiO₂. Upon sulfidation, MoS₂ or WS₂ with Ni or Co promoter at the edges are generated as the active phases^[38]. Various models are used to describe the active phases and are accorded to belong to either Type I [Ni(Co)MoS I] or Type II [Ni(Co)MoS II]. Type I contains the monolayer MoS₂ that maintains a strong interaction with Al₂O₃ via chemical bonds such as (Ni)Mo-O-Al, forming tetrahedral Mo oxides that are difficult to reduce and sulfide. Type II represents weaker interactions with Al₂O₃ via van der Waals-type interactions with suppressed dispersion, MoS₂ layers with better stacking, increased cathedral Mo oxides that are easier to reduce, and complete sulfidation that leads to better HDS activity^[38]. The role of the promoter is to donate electrons, promote dispersion, and reduce the interaction between the support and the metal (active metal)^[82]. With a better understanding of the Co(Ni)Mo(W)S structure, it has been widely recognized that the HDS activity can be promoted by tuning the morphology of the active phase, the interaction between the active metal and the support, adjusting the properties of the supports (surface area and porosity, acidity), and using additives and chelating ligands^[36].

Metal precursors have been varied during synthesis of HDS catalysts to come up with enhanced catalytic activity. Traditional metal salts are being replaced by other metal precursors, such as ammonium heptamolybdates, and cobalt salts, such as heteropoly compounds (HPCs). Dawson, Anderson, Keggins, and Strandberg HPCs as precursors for CoMo catalysts were found to produce catalysts with higher activity due

to good homogenous distribution of the active phases on the surface of the support and more metal loading compared to conventional compounds^[92]. Anderson-type HPCs $\{\text{Mo}_{12}\text{O}_{30}(\mu_2\text{-OH})_{10}\text{H}_2[\text{Co}(\text{H}_2\text{O})_3]_4\}$ contain both Co and Mo atoms in their molecular structure, and using them as precursors leads to a higher concentration of active CoMoS phase on the support material and increased HDS activity due to intimate contact between Co and Mo atoms^[92]. Various additives have also been investigated to improve the activity and selectivity of conventional HDS catalysts; P, F, B, Cl, Zn, Mg, Li, Na, K, Ca, and rare-earth metals, with P and F being the most prominent^[90,93,94].

Improved hydrodesulfurization catalysts

HDS has never been a challenge due to the high reactivity of most S-containing compounds until recently due to the need to achieve deep desulfurization through improved desulfurization of refractory S-containing compounds and the need to accommodate harsher feedstock that have higher concentrations of S-containing compounds, especially the refractory compounds^[80,95]. Transition metal phosphides^[96], silicides, and carbides, nitrides have been proposed as deep HDS catalysts^[95,97]. Carbides have drawn much attention due to their unique catalytic properties for deep HDS such as the resistance to sintering at high temperatures during HDS reactions; they have strong interactions with heteroatoms (S, N) and inertness towards C-C bond scission, resulting in high selectivity, high hydrogenation activity with their noble metal-like catalytic properties^[95,98,99]. Doping non-metal atoms into metal phosphides results in the formation of isolated sites and electronic modification that enhances HDS activity and stability^[95]. However, metal phosphides suffer from long-term stability and are prone to deactivation due to their strong affinity with the adsorbates, especially at high temperatures^[99]. Several authors have shown that transition metal phosphides (MoP, Ni₂P, and Co₂P) as an active phase are found to be one of the active catalysts in HDS catalysts^[100]. The Metal phosphide catalysts exhibit higher HYD activities as compared to Co(Ni)Mo(W)S catalysts and possess high catalytic activity in HDS reactions, thus increasing HDS activity^[95,97,100]. Ni₂P catalysts display a strong resistance to deactivation by sulfur^[38,97]. Cellia *et al.* found that metal phosphides change the acid-base properties of the support, which affects the dispersion of the active phase, resulting in improved catalytic activity^[101]. Noble metals (Pd, Pt, Ru, Re, Rh, and Ir) have also been widely investigated for deep HDS catalysis due to their high hydrogenation and hydroisomerization activities, Pd and Pt being the most prominent^[36,102,103]. Weise *et al.* compared an unpromoted Pt catalyst with a Pt-doped industrial CoMo catalyst and observed a 46% increase in activity in the latter, attributing the increase in catalytic performance to the incorporation of Pt atoms on the terminal edges and corner sites of CoMo^[104]. Pt reduced the binding energy of sulfur, favored the formation of CUS, and created sites that are favorable to the adsorption of sterically hindered molecules such as 4,6-DMDBT^[104,105].

We recently reported higher HDS of DBT due to a good synergistic effect between Rh promoter and Mo and more MoS₂/RhMoS phases when we tested a series of RhMo-x/Al₂O₃ catalysts with different chelating ligand ratios (x = ethylene diamine, tetraacetic acid, acetic acid, citric acid)^[104,105]. We attributed high activity to electron donation from Rh to the Mo conducting band, weakening Mo-S bonds and facilitating the formation of CUS [Figure 3]. However, the high cost and vulnerability of noble metals discourage their industrial application as HDS catalysts.

More cost-effective and abundant metals to replace the conventional active and promoter metals, especially Mo and W, are also being sought due to the increasing demand, low crust abundance, high mining cost, and environmental toxicity of these metals^[36,38,106]. Ti, V, Nb, and Fe have been tested as potential HDS catalysts^[36]. Iron has attracted the most attention due to its low cost, high crust abundance, and environmental friendliness^[36]. Fe has some level of hydrogenation activity as it is known to have lattice structures and an unfilled d-electron layer, similar to metal species that are used in conventional

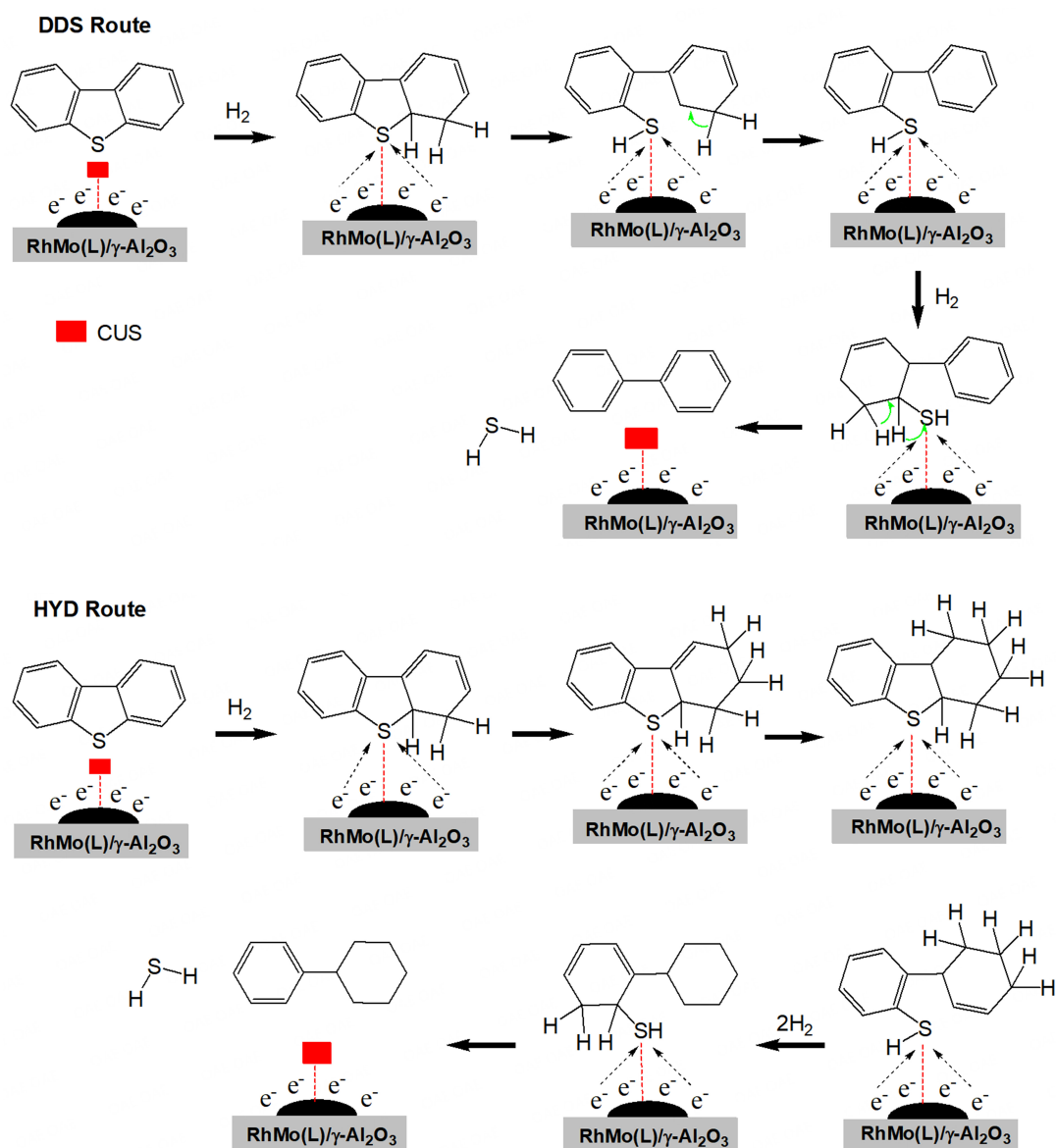


Figure 3. Proposed Mechanisms of DDS and HDS reactions on RhMo chelated Catalysts in HDS of DBT^[104,105]. DBT: Dibenzothiophene; DDS: direct desulfurization; HDS: hydrogenation-desulfurization.

hydrotreating catalysts (Co, Ni, Mo, Pt, and Pd)^[36]. Although Fe is common in processes such as ammonia synthesis, direct coal liquefaction, Fischer-Tropsch synthesis, and HDO, there are few studies where Fe was tested as an active metal in HDS catalysts. Iron-based catalysts are generally considered to have poor HDS activity, with iron sulfide having much lower than Mo and W sulfide, which is associated with Pauling $d\%$ of metals that lead to the different strength of the metal-sulfur covalent bond and sulfidation degree of TMS^[36]. Li *et al.* reported improved activity of Fe-based catalysts after incorporating zinc as a promoter^[107]. The presence of Zn in the catalyst attributed excellent electron donation to Fe, thereby forming a new active phase (FeZnS_x)^[95,107]. The addition of Zn also resulted in the generation of more sulfur vacancies^[37]. The study also emphasized the major role played by suitable support materials in enhancing the catalytic activity of Fe-based catalysts. It was found that the incorporation of nitrogen on the carbon support provides

unique electronic properties such as promoting the dispersion of Fe, improving its electron-donating capabilities to the active metal (Fe), greatly weakening the Fe-S bond and promoting the formation of CUS, thereby enhancing the HDS activity^[95,107]. Typical catalysts that have been developed for HDS are presented in Table 2.

Active and promoter mineral materials in hydrodenitrogenation catalysts

Conventional hydrodenitrogenation catalysts

The C(sp²)-N bond is very strong and makes hydrogenation of at least the N-heterocyclic ring in aromatic nitrogen-containing heterocycles a prerequisite to achieving C-N bond breaking, unlike in HDS where pre-hydrogenation of the S-ring is a possible pathway but not a prerequisite for C-S bond breaking^[93,116-118]. As such, HDN catalysts need to be bifunctional, having both hydrogenation sites and hydrogenolysis sites. The most common HDN catalysts are the conventional Mo and W sulfides promoted by Ni sulfides, e.g., Ni/Mo-Al₂O₃ and Ni/W-Al₂O₃^[8,119]. Although these catalysts are prominent in hydroprocessing, their HDN activity is poor^[21]. These catalysts require intensive operating conditions to hydrogenate the heterocyclic rings, often causing unnecessary saturation of the carbocyclic rings to achieve C-N cleavage^[119]. CoMo, NiMo, and NiW catalysts are significantly more active for HDS than for HDN at any given reaction condition^[22]. N-containing compounds are less reactive to hydroprocessing and consume more hydrogen, and the process is more energy-intensive^[22]. Higher energies are required to break C-N bonds. Heterocyclic N-containing compounds, such as quinoline and indole, are more difficult to remove, require more severe conditions, and are predominant in heavier feeds^[118]. HDN becomes more difficult when shifting from light to heavier feeds with higher boiling points and complexity, e.g., shale oil- and coal-derived oils^[11,120]. The development of better HDN catalysts becomes even more important considering the growing need to process heavy and low-quality feeds rich in highly refractory N-containing compounds^[13,14,121]. Besides that, all acidic catalysts (cracking, reforming, fluid catalytic cracking, hydrocracking, HDS, hydrogenation, and isomerization) are vulnerable to inhibition/poisoning by nitrogen-containing compounds, and good HDN catalysts will be important for HDN pre-treatment of feedstocks^[7,13,120,122].

Improved hydrodenitrogenation catalysts

Various transition metal oxides, sulfides, phosphides, borides, nitrides, and carbides have been investigated as HDN catalysts^[21,123,124]. Sulfides, nitrides, and carbides show good potential for HDN due to their ability to exchange S, N, or C, and they can adapt their chemical composition to that of the feed during reactions to form highly active phases^[125]. Al-Megren *et al.* demonstrated using a pyridine stream that the HDN activities of bimetallic (CoMo) carbide, oxide, nitride, and sulfide catalysts are of the order: CoMoC_x ~ CoMoN_x ~ CoMoO_x > CoMoS_x, while their stability follows the order: CoMoC_x > CoMoN_x > CoMoO_x with decrease in activities over time^[124]. Qiu *et al.* found the α-phase of Mo₂C to have the highest selectivity and conversion of quinoline compared to the β-phase^[126]. Better HDN potential has been demonstrated using metal phosphides, borides, and nitrides. Fang *et al.* investigated the effect of different metals, metal loading, ratio of metal to phosphorous, and other catalyst preparation methods on the activities of transition metal phosphides^[21]. The performance of transition metal phosphides was found to be significantly higher than metal sulfides. High activity was obtained from a NiP catalyst, with further improvement of activity being obtained with the addition of small amounts of Co or Fe and a change of support materials^[21]. This was attributed to Ni preferentially occupying the active hydrogenation square pyramidal M(2) site^[21]. During simultaneous HDS and HDN, the overall activity of metal phosphides followed the order of Ni₂P > WP > MoP > CoP > Fe₂P^[13]. Transition metal phosphides were tested for HDS (dibenzothiophene) and HDN (quinoline), and their activities followed the order Fe₂P < CoP < MoP < WP < Ni₂P. Ni₂P/SiO₂ had higher activity compared to the commercial Ni-Mo-S/Al₂O₃ (HDS 98% vs. 78% and HDN 80% vs. 43%) and commercial Co-Mo-S/Al₂O₃ (HDS 85% vs. 80%)^[23]. It was also demonstrated that HDN using Ni₂P involves activation at carbon positions α and β to nitrogen atoms in contrast to sulfides where activation only occurs

Table 2. Typical catalysts for HDS reactions

Catalyst	Composition			Feedstock	Reaction conditions	Comments	Ref.
	Active material(s)	Promoter(s)/Additive(s)	Support				
MoS ₂	MoS ₂	-	-	DBT and/or Q in decane	Batch, 340 °C, 3 MPa H ₂ pressure, copper scrubber for H ₂ S	Strong hydrogenation function, quinoline inhibitory on HDS via hydrogenation pathway.	[108]
CoMo/Al ₂ O ₃	Mo	0.57wt.%, 1.21wt.%, 2.18wt.%, 2.68wt.%, 3.35wt.% Co, 8.17wt.%, 8.27wt.%, 8.35wt.%, 8.37wt.%, 8.45wt.% Mo	Al ₂ O ₃	DBT	Batch Parr reactor, 593 K, 1,250 psi, Time on stream = 4 h	Increased activity in Co-promoted catalysts due to cobalt sulfide upon addition of Co/Al ₂ O ₃ to Mo/Al ₂ O ₃ or CoMo/Al ₂ O ₃ catalysts. Both MoS ₂ and CoMoS phases were promoted.	[109]
CoMo/Al ₂ O ₃ -TiO ₂	MoS ₂	13wt% of MoO ₃ and 3.3wt% of CoO	Al ₂ O ₃ -TiO ₂	Pyrolysis gasoline	Fixed-bed, 400 °C, 1 atm	Ti increased the surface acidity and improved the reductive behavior of the tetrahedral and octahedral Mo species. CoMo/Al ₂ O ₃ -TiO ₂ with 10wt.% titania removed over 96% of sulfur-containing molecules in Pygas with improved product quality.	[60]
CoMoP/γ-Al ₂ O ₃	Mo	12.5wt.% ± 0.2wt.% of Mo, 3.5wt.% ± 0.1wt.% of Co and 1.5wt.% ± 0.1wt.% of P	γ-Al ₂ O ₃	DBT, quinoline and naphthalene	Flow glass reactor, 280 °C, 3.5 MPa, WHSV = 80 h ⁻¹	Hydrothermal treatment of a flash calcined gibbsite makes it possible to obtain hydrotreating catalysts with the highest or the same activity in the HDS and HDN of fuel mixture compared to catalyst supported on alumina obtained through the precipitation of pseudoboehmite from aluminum nitrate.	[35]
CoMo/MWCNT-citr, CoMoS/Al ₂ O ₃ -citr	Mo	12.0wt.% of Mo and 3.2wt.% of Co, Ctr	Al ₂ O ₃ and MWCT	DBT	Fixed bed, 280 °C, 3.5 MPa, LHSV 20.0 h ⁻¹	CoMo/MWCNT-citr catalyst had the highest HDS activity due to higher sulfidation degree, higher CoMoS phase content, and improved dispersion of sulfide components.	[79]
CoMoS/C@γ-Al ₂ O ₃	MoS ₂	3.2wt.% Co and 12.0wt.% Mo	C@γ-Al ₂ O ₃	DBT	Fixed bed flow, 270 °C, 3.5 MPa, LHSV = 20.0 h ⁻¹	Higher dispersion of sulfided components and enhanced promotion of MoS ₂ by Co.	[46]
CoMoS ₂ /ZSM-5	MoS ₂	Co, 10.7wt% Mo, EDTA	ZSM-5	4,6-DMDBT	High-pressure stirred reactor, 573-593 K, 2-5.0 MPa	Multi-stacked MoS ₂ nanocrystallites on CoMoS ₂ /MZSM-5 provide more available sulfur vacancies to facilitate the DDS pathway and catalyze efficiently the hydrogenation.	[110]
CoMo/NDC@Al ₂ O ₃	Mo	18% (mass) MoO ₃ and 4% (mass) CoO	NDC@Al ₂ O ₃	DBT, 4,6-DMDBT, and Dagang diesel	Batch reactor, 300 and 320 °C, 6 and 7 MPa, LHSV = 1 h ⁻¹ , H ₂ /Oil = 200:1	The introduction of NDC reduced the interaction between the support and active components. Improved dispersion of active phase and sulfidation degree of Mo by 21.8% compared to the CoMo/γ-Al ₂ O ₃ .	[111]
Sulfided NiMo/γ-Al ₂ O ₃	8wt.% Mo	3wt.% Ni on	γ-Al ₂ O ₃ (Condea, pore volume 0.5 cm ³ ·g ⁻¹ , specific surface area 230 m ² ·g ⁻¹)	4,6-DMDBT vs. presence of 2-methylpyridine and 2-methylpiperidine	Fixed bed, 340 °C and 5 MPa	DDS and HYD inhibited, 2-methylpiperidine > 2-methylpyridine, no significant contribution from change to aromatic solvent	[112]
NiMo/Al ₂ O ₃	MoS ₂	3.0wt.% NiO and 13.0wt.% MoO ₃	Al ₂ O ₃	DBT	Fixed-bed, 240, 260, and 280 °C, 4 MPa, LHSV = 20 h ⁻¹	Ni-Al ₂ O ₃ interaction enhances the availability of surface nickel atoms to form more NiMoS phase and improves the microstructure of MoS ₂ .	[36]

NiMo	MoS ₂	Ni	-	DBT	Batch reactor, 340 °C, 50 bar	Both catalysts exhibited good performance (lp-NiMoS, 95.8%, and hp-NiMoS, 98.6% DBT conversion), with hp having the highest due to the formation of more NiMoS.	[113]
NiMo/SBA-15	Mo (6.09wt.%, 10.53wt.%, 11.08wt.%, 15.75wt.%)	Ni (1.65wt.%, 3.04wt.%, 2.59wt.%, 2.63wt.%)	SBA-15	DBT	Batch reactor, 320 °C, 3 and 6 MPa	One-pot synthesis promoted the generation of dispersed shorter MoS ₂ slabs with desirable average stacking numbers.	[114]
NiW/Al ₂ O ₃	WS ₂	Ni, P WO ₃ (20wt.%), NiO(4wt.%) and P ₂ O ₅ (2wt.%)	Al ₂ O ₃	DBT	Fixed-bed, 220-280 °C 4.0 MPa, LHSV = 10-60 h ⁻¹	Addition of P improved the availability of surface Ni atoms, P weakened metal support interaction, and enhanced the promotion of NiWS.	[80]
NiMoW/Ti-HMS	MoS ₂ and WS ₂	3.8wt.%, 13.8wt.% and 17.3wt.% of NiO, MoO ₃ and WO ₃	Ti-HMS mesoporous	DBT	Batch reactor, 320 °C, 58.6 bar	More CUS formed, increased both DDS and HYD and high dispersion.	[50]
NiTMo-x/Al ₂ O ₃	Mo	Ni, tetradecylamine; for NiO and MoO ₃ (3.6wt.% and 16.9wt.%, and 3.5wt.% and 16.8wt.%)	Al ₂ O ₃	4,6-DMDBT	Fixed-bed, 360 °C, 4.0 MPa, LHSV = 15.0 h ⁻¹ , time on stream = 6 h	NiTMo-2.0/Al ₂ O ₃ had the most corner and edge S vacancies, exhibited the highest reaction rate constant, and had the highest DDS ratio of 99.5% in HDS of 4,6-DMDBT.	[86]
Ni ₂ P@C, Ni ₂ Si@C, and NiS ₂ @C	-	P, Si	Carbon	DBT	Trickle fixed-bed, 260 and 360 °C, 3.0 MPa	HDS activity: Ni ₂ P@C > Ni@C ≈ Ni ₂ Si@C > NiS ₂ @C. Ni ₂ P@C shows outstanding stability during the long-term reaction.	[95]
Ni ₂ -xRuxP/SiO ₂	-	Ru, Ni	SiO ₂	4,6-DMDBT	Fixed bed, 533-593 K, 3.0 MPa	Ni _{1.85} Ru _{0.15} P/SiO ₂ catalyst 15 and 6 times more active (on a mass basis) than Ni ₂ P/SiO ₂ and Ru ₂ P/SiO ₂ catalysts. Ru resulted in P surface enrichment and lowered the temperature of precursor reduction.	[97]
Rh-M-P (M = Ru, Pt, Ir)	Rh (5.0 and 4.85wt.%), Pt	Ru (0.15wt.%), Pt (0.28wt.%), Ir, P (5.0wt.%, 1.51wt.%, and 3.0wt.%)	SiO ₂	Th and 4,6-DMDBT	Fixed bed, 350 °C, 0.1 and 4.0 MPa	Rh-Pt-P catalyst had the highest HDS activity among Rh-M-P catalysts.	[115]
Pt-Co-Mo	Mo	Pt, 16wt.% Mo and 3.5wt.% Co	-	Diesel	Fixed bed, 355 °C, 30 bar, LHSV = 1.5 h ⁻¹ , Time on steam = 24 h	The addition of ppm levels of Pt to a conventional Co-Mo-S catalyst boosted HDS activity by up to 46%. Pt is suggested to reduce the sulfur binding energy and increase the abundance of CUS. Pt is speculated to create sites for favorable adsorption of sterically hindered molecules.	[104]

CUS: Coordinatively unsaturated sites; DBT: dibenzothiophene; DDS: direct desulfurization; HDN: hydrodenitrogenation; HDS: hydrogenation-desulfurization; HYD: hydrogenation; LHSV: liquid hourly space velocity; MWCT: multi-walled carbon nanotube; WHSV: weight hourly space velocity ; 4,6-DMDBT: 4,6-dimethyldibenzothiophene.

at the β position. HDN activities of silica-supported phosphide catalysts (Co₂P/SiO₂, MoP/SiO₂, WP/SiO₂, CoMoP/SiO₂, and NiMoP/SiO₂) were tested using o-methylaniline, and MoP/SiO₂ was found to have the highest activity^[127]. Wagner *et al.* showed that of the Ni phosphide phases, HDN activity of quinoline increases in the order Ni₂P > NiO > Ni₁₂P₅^[128]. Transition metal borides were also found to have good hydrogenation activity and strong resistance to sulfur,

making them good candidates for HDN of N-containing compounds^[129]. Rhenium sulfide was found to have the highest HDS and HDN rates compared to Rhenium nitride and Re metal. ReN_2 was found to have better HDN activity compared to HDS, but its surface transformed back the Re metal after the reaction^[130]. MoN was found to be about an order of magnitude more active than a commercial sulfided Co-Mo/ Al_2O_3 in the HDN of pyridine with higher selectivity for C-N hydrogenolysis compared to C-C hydrogenolysis^[131]. Lee *et al.* reported rapid hydrogenation of quinoline over Mo_2N ^[132].

Based on periodic trends in Figure 2B, noble metals are the best candidates for HDN activity. Their high HDN activity is accompanied by a lower tendency for coke formation at milder conditions compared to sulfided CoMo catalysts^[24]. Additionally, synthesis of noble metal catalysts with non-alumina supports is easy, where alumina has to be avoided^[24]. Noble metals are, however, very expensive, and they are vulnerable to inhibition and/or poisoning^[120]. For example, good HDN activity has been reported for a Pt catalyst, but sulfur inhibition has been cited as a major challenge^[8]. Contrastingly, alumina-supported metallic Ni, Rh, and Ru showed high HDN activity but suffered deactivation due to H_2S , except for Pt, which maintained suitable activity^[133]. HDN of quinoline was very high using 1% Ir in Al- and Ga-modified silica catalysts due to Ga and Al having Bronsted and Lewis acid sites that work in synergy to give high activity alongside the good dispersion of the catalytic sites^[134]. However, appreciable deactivation was observed in the catalysts. On the other hand, ReS_2 was among the most active transition metal sulfides, but its activity was not always better than industrial CoMo/ Al_2O_3 and NiMo/ Al_2O_3 , and the promoting effect of Co and Ni was found to be low compared to the Mo catalysts^[135]. The addition of $\text{Ru}_3(\text{CO})_{12}$, a precursor to catalysts that cleave C-N bonds in amine transalkylation reactions, to a commercial CoMo HDN catalyst resulted in significantly improved activity^[4]. Carbon and nitrogen can be incorporated in interstitial positions (lattice) of early transition metals (groups 4 to 6), resulting in some pure transition metal carbides and nitrides (e.g., Mo and W carbides and nitrides) that have metallic properties that resemble noble metals^[93,99]. The addition of carbon was reported to cause higher hydrogenation properties compared to the addition of nitrogen^[99]. Transition metal oxynitrides and oxycarbides are reported to act as bifunctional catalysts through their metallic and acidic active sites, and HDN of indole can occur without pre-hydrogenation of the aromatic ring. They are efficient at activating dihydrogen and N-containing molecules^[125].

Physical properties of the catalysts, e.g., particle size and porosity, also have an influence on catalyst performance^[11]. The morphology of the sulfide material (e.g., curvature and stacking of layers) was found to influence the catalyst activity in bulk metal sulfides such as MoS_2 and WS_2 ^[121]. The order of impregnation of the metal precursors on the support (e.g., Mo then Co or Ni, or vice versa) and calcination was found to have a significant influence on the activity of the final sulfided catalyst. Impregnating with Mo first was found to give catalysts with an invariably higher activity^[11,93]. Mixing metals by closely interlinking them using sulfur bonds in HDN catalysts results in a significant increase in activity compared to analogous conventionally prepared catalysts^[136]. Table 3 comprises a range of catalysts that have been developed for HDN.

Active and promoter mineral materials in hydrodeoxygenation catalysts

Conventional hydrodeoxygenation catalysts

Conventional alumina-supported CoMo and NiMo catalysts are usually applied in HDO at moderate temperatures (300-600 °C) and high pressure (7-20 MPa)^[147]. The oxygen is removed through a series of reactions, such as decarboxylation, saturation of unsaturated compounds, and C=O via hydrogenation, cleavage of C-O bonds *via* hydrogenolysis, and cleavage of heavy molecular weight compounds to lighter molecular weight compounds *via* hydrocracking^[148-150]. Hydrocarbon percentage yields were similar in the HDO of waste cooking oil using conventional sulfided catalysts (NiMo/ Al_2O_3 , CoMo/ Al_2O_3 , and

Table 3. Typical hydrodenitrogenation catalysts

Catalyst	Composition			Feedstock	Reaction conditions	Comments	Ref.
	Active material(s)	Promoter(s)/Additive(s)	Support				
CoMo/Al ₂ O ₃	12.5wt.% Mo	3.5wt.% Co 1wt.% P 1wt.% B	Boehmite HQ102 B produced in China (292 m ² ·g ⁻¹ ; pore volume 1,02 cm ³ ·g ⁻¹ ; pore diameter 140 Å)	Straight-run diesel fuel: 0.383% of S; 192 ppm of N; density of 0,861 g/cm ³ ; boiling range = 207-380 °C ("GazpromneftOmsk NPZ", Omsk, Russia)	31 cm ³ catalyst mixed 1:2 with SiC, 360 and 370 °C, 3.8 MPa, H ₂ /feed = 544 nm ³ /m ³ , LHSV = 2.5 h ⁻¹	CoMoS phase content increased with increasing concentration of P, but more than 2wt.% of P leads to a decrease of SSA and pore volume. Increased activity is attributed to increased surface concentrations of P(OH) or B-OH groups, which adsorb N compounds before they migrate to the sulfide active component.	[137]
Nitrided 12.5% Mo/Al ₂ O ₃	Mo	-	γ-Alumina xerogel	0.25wt.% carbazole in xylene	2.0 g catalyst in a stainless steel fixed-bed microreactor, feed flow= 20 mL·h ⁻¹ , H ₂ flow = 74.4 μmol·s ⁻¹ , 573 K, 10.1 MPa	High hydrogenation activity in carbazole HDN. The activity of the nitrided catalysts for the hydrogenation in carbazole HDN is not related to surface acidity but rather to the reduced molybdenum ions Mo ²⁺ and Mo ⁰ on the surface of the molybdenum nitrided catalysts.	[138]
Bulk molybdenum carbide (Mo ₂ C)	Mo	-	-	2.5wt.% of indole dissolved in decaline or 0.4wt.% carbazole in o-xylene	0.8 g of catalyst in SiC (SiC/Mo ₂ C = 5:1), 613 K, 60 bar, H ₂ /feed ratio of 600 and contact times (t _c) 0.13-1.07 s	High HDN is maintained even in the presence of small amounts of S (50 ppm). Bulk Mo ₂ C behaves similarly to that of a noble metal catalyst. Direct HDN is predominant during the early conversion percentages, while at high conversions, the HYD route is followed.	[129, 139]
α-MoC _{1-x}	Mo	-	Specific surface area (107.6 m ² ·g ⁻¹)	-	-	Higher SSA, activity, and selectivity than β-Mo ₂ C	[126]
Molybdenum carbide (Mo ₂ C) vs. Tungsten carbide (W ₂ C)	Mo or W	-	-	0.4wt.% of carbazole in o-xylene	Downflow fixed bed microreactor, 553 and 653 K, 6 MPa, H ₂ /feed ratio of 600, contact times (t _c) = 0.07-0.8 s	HDN via hydrogenation for both catalysts. Both are bifunctional catalysts (hydrogenation and isomerization). Both reactions are more significant in W ₂ C, but the activity of Mo ₂ C is higher than that of W ₂ C.	[140]
Silica-supported nickel phosphide (Ni ₂ P) and Ni-rich bimetallic phosphide catalysts [25wt.% Ni ₂ P/SiO ₂ , Fe _{0.03} Ni _{1.97} P/SiO ₂ and Co _{0.1} Ni _{1.9} P/SiO ₂]	Ni or Fe or Co	P (ratio 0.9 to 1.0 with metal)	Silica (Cab-O-Sil, M7D)	1,000 ppm carbazole + 500 ppm dodecane in 39.85wt.% p-xylene/decane or 3,000 ppm benzothiophene + 1,000 ppm carbazole + 500 ppm dodecane in 39.55wt.% p-xylene/decane.	0.25 g catalyst mixed with quartz flakes to a total volume of 5 mL in a fixed bed continuous flow reactor, 548-673K, 3.0 MPa, feed flow = 5.4 mL·h ⁻¹ , H ₂ flow = 50 mL·min ⁻¹	Higher carbazole HDN conversion in all catalysts compared to commercial Ni-Mo/Al ₂ O ₃ . Metal phosphides are much higher (92%-98%) vs. Ni-Mo/Al ₂ O ₃ (75%-84%). Carbazole HDN on metal phosphides inhibited by DBT co-feeding Ni ₂ P/SiO ₂ and Ni-rich bimetallic phosphide catalysts maintained their activities. Metal phosphides favored ring-opened and ring-contracted products, indicating the presence of metal and Brønsted acid sites on the catalyst surfaces.	[141]
Transition-metal phosphides (Co ₂ P, Ni ₂ P, MoP, WP, CoMoP, NiMoP)	Ni or Mo or W	Ni or Co, P	-	o-propylaniline in n-octane	0.05-0.4 g catalyst diluted with 8 g SiC, continuous-flow microreactor, 643 K, 3 MPa	MoP and WP > Ni ₂ P and NiMoP > Co ₂ P and CoMoP. All catalysts except for WP lost their activity in the presence of H ₂ S, being irreversible in the case of Ni ₂ P.	[142]

CoMoP/Al ₂ O ₃ and NiMoP/Al ₂ O ₃	Mo	Co or Ni	Al ₂ O ₃	-	-	NiMoP has stronger hydrogenating power than CoMoP.	[143]
Zeolite supported Nickel phosphides (NixPy)	5wt.% Ni	P (3:0 P/Ni)	Commercial Na ⁺ Y and NH ₄ ⁺ Y zeolites (Molecular sieves, powder, Si/Al ratio: 2.56) or zeolite (SiO ₂ /Al ₂ O ₃ mol ratio: 30:1, powder form)	1 mL 10vol.% (14.1wt.%) quinoline in dodecane solution	50 mg catalyst in 1 g of silica gel in 6 mL stainless steel batch reactors, 400 °C, 40 bar	HDN activity: Ni ₂ P > NiO > Ni _{1.95} P ₅ . The activity of catalysts comparable to commercial 5wt.% Pd/C, NiCoMo/Al ₂ O ₃ and NiMo/CeO ₂ catalysts.	[128]
Ni ₂ P/MgAlO	60% Ni	Phosphorous	MgAlO	1.72% DBT (3,000 ppm S), 0.185% quinoline (200 ppm N), 5% tetralin and 0.5% n-octane in n-tetradecane	Fix-bed reactor, 513 to 613 K, 3.1 MPa, LHSV = 2 h ⁻¹ , H ₂ /oil ratio = 1,500 (v/v)	MgO/Al ₂ O ₃ ratios had no influence on the intrinsic activity of Ni ₂ P. Ni ₂ P/MgAlO with the MgO/Al ₂ O ₃ ratio of 3 showed the highest activities. 92.6% conversion of DBT at 513 K Ni ₂ P/MgAlO catalysts. 67.6% conversion of tetralin at 613 K, significantly higher than other catalysts (46.1%-58.6%).	[144]
Ni-rich bimetallic phosphides	Mo and Ni	P	-	2wt.% quinoline and 1wt.% DBT in decalin	Simultaneous HDN (quinoline) and HDS (DBT) in a fix-bed reactor. 1 g catalyst mixed with 9 mL quartz sand, 320-380 °C, 3 MPa, WHSV = 6 h ⁻¹ , H ₂ /feed flow ratio of 500:1	Increase in HDN and HDS conversions with increasing temperature, approaching 90% and 100% at 380 °C, higher than the commercial MoNiW/Al ₂ O ₃ catalyst. Mo _{0.05} Ni _{1.95} P showed the highest activity in simultaneous HDS and HDN compared to Co _{0.05} Ni _{1.95} P, Mo _{0.05} Ni _{1.95} P, Fe _{0.05} Ni _{1.95} P and W _{0.05} Ni _{1.95} P. Catalyst activity is greatly reduced by quinoline.	[21]
NiB alloy	87.2% of nickel	7.1% of boron	-	0.08% carbazole (100 ppm N) or 0.08% carbazole and 0.17% 4,6-DMDBT (300 ppm S) in o-xylene.	Down-flow fixed-bed microreactor, simultaneous HDN/HDS (0.8 g catalyst) or HDN alone (0.2 g catalyst) in SiC (1:5), H ₂ flow = 60,360 cm ³ .min ⁻¹	Carbazole HDN takes place mainly on the Ni metallic phase, with bicyclohexyl as the main product. Decomposition of catalyst noted during the 100 h of use. Catalyst activity is lower for HDS/HDN due to partial sulfidation of the catalyst.	[129]
W/Al ₂ O ₃	20wt.% WO ₃	6wt.% P ₂ O ₅	Al ₂ O ₃ GirdlerT-126, surface area 188 m ² .g ⁻¹ , pore volume 0.39 cm ³ .g ⁻¹ , particle size 0.15-0.25 mm	Gas oil and pyridine	Flow trickle bed microreactor, 3.5 g catalyst in SiC, LHSV = 8.8 h ⁻¹ , H ₂ /liquid feed of 400 v/v; 598, 623, and 648 K	Simultaneous HDS/HDN. P ₂ O ₅ increases the amount of reducible tungsten oxide species by promoting the formation of octahedral polytungstates, has little effect on the lateral growth of the WS ₂ slabs but significantly increases the average number of layers, enhances both HDS and HDN activities but more effectively for HDS than HDN.	[20]
Platinum-doped tungsten carbide (W ₂ C-Pt)	W	0.3wt% Pt	-	0.17% 4,6-DMDBT (300 ppm S) and 0.08% carbazole (100 ppm N) in o-xylene	350 °C, 6.0 MPa, molar H ₂ /feed ratio = 600	Simultaneous HDS and HDN. W ₂ C, Pt-W ₂ C, W ₂ C-Pt compared. W ₂ C-Pt has the highest conversions 55% and 100% of conversion for HDS and HDN, while W ₂ C, Pt-W ₂ C are not far at around 27% and 90% for HDS and HDN. Pt increases HDN activity of W ₂ C-Pt. Increased HDS conversion after t _c > 0.31 s when HDN is complete is attributed to earlier completion of HDN.	[15]

W ₂ C, Pt-W ₂ C and W ₂ C-Pt	W ₂ C and Pt	-	W ₂ C synthesized from temperature programmed reaction of WO ₃ (Fluka 99.9% pure) with 10vol.% CH ₄ /H ₂ gas mixture.	0.17% 4,6-DMDBT (300 ppm S) and 0.08% carbazole (100 ppm N) in o-xylene	1:5 catalyst SiC, 0.25 g catalyst, 350 °C, 6.0 MPa, molar H ₂ /feed ratio of 600	Simultaneous HDS and HDN. W ₂ C exhibits both HDS and HDN activity. Addition of Pt showed no effect on HDS activity at short contact time (t _c < 0.21 s), unlike HDN activity, where a significant increase was observed. HDS only increased towards the completion of HDN, indicating possible inhibition of N on Pt. W ₂ C and Pt-W ₂ C had similar activity (up to 27% HDS and 90% HDN activity) compared to W ₂ C-Pt (55% HDS and 100% HDN activity). The addition of Pt prior to W ₂ C synthesis results in no increased activity.	[15]
Re/Al-SBA-15 and Ni-Re/Al-SBA-15	5wt.% Re	1wt.% Ni	SBA-15 572 m ² /g, 0.5 cm ³ /g, Dp 6.96 nm	2.5wt.% of o-toluidine in cyclohexane	Fixed-bed flow reactor system, 4 cm ³ catalyst, 673-723 K, H ₂ flow = 50 cm ³ .min ⁻¹ , atmospheric pressure	The highest HDN activity in 5wt% Re/Al-SBA-15(10) is attributed to the fine dispersion of Re over the support and successful incorporation of Al into SBA-15, which enhances the strong metal-support interactions and formation of moderate acid sites. Ni-Re/Al-SBA-15 had higher activity due to Ni promoter effects.	[145]
Mo-Ir/Al ₂ O ₃	Mo	0.34wt.%-0.53wt.% Ir	γ-alumina CS 331-1 SA 255 m ² .g ⁻¹ , pore volume 0.76 mL.g ⁻¹ , particle size of 0.16-0.32 mm	220 ppm of pyridine and 240 ppm of thiophene.	Fixed bed, 0.05-0.2 g catalyst, 320 °C, 20 bar, H ₂ flow = 0.4 mol.h ⁻¹	Simultaneous HDN/HDS. The addition of Ir to Mo/Al ₂ O ₃ led to increased reducibility of the Mo phase and enhancement of HDN and HDS activities, especially HDN, where a synergetic effect resulted in 3 times more activity at loadings of about 0.34wt.%-0.53wt.% Ir. HDN/HDS selectivity of modified catalysts was higher than the selectivities of individual Ir and Mo catalysts.	[146]
Pt/Al ₂ O ₃ and Pt/SiO ₂ -Al ₂ O ₃	Pt	-	Alumina (Condea, Sp - 180 m ² .g ⁻¹) or silica alumina (Condea, 40% of SiO ₂ , Sp - 374 mE.g ¹)	-	-	Five times more active than NiMo/Al ₂ SO ₃ , sulfur inhibition poses a challenge.	[8]

DBT: Dibenzothiophene; HDN: hydrodenitrogenation; HDS: hydrogenation-desulfurization; HYD: hydrogenation; SSA: specific surface area; WHSV: weight hourly space velocity; 4,6-DMDBT: 4,6-dimethyldibenzothiophene.

NiW/Al₂O₃)^[151]. HDO of methyl phenols has been achieved using an alumina-supported CoMo catalyst at an even lower pressure of 2.85 MPa and 300 °C^[152]. The influence of conventional promoters in driving HDO reactions has also been discussed in the literature, e.g., Co being more HDO selective compared to Ni and octahedral Ni species being more active than tetrahedral Ni species in NiMoS/Al₂O₃^[153,154]. Generally, oxygen-containing compounds are highly reactive, but phenols and benzofurans tend to be less reactive, and these are found in higher concentrations in coal-derived oils^[7]. The need to migrate from alumina-supported catalysts due to their vulnerability to dealumination, especially for high oxygen content feedstocks such as biodiesel, and the need to effectively hydrodeoxygenate the less reactive phenols and benzofurans has been driving further development of HDO catalysts. Bio-oils of very low sulfur content are also known to cause poor regeneration of catalyst active sites, affecting catalyst performance^[155-160]. Leaching of sulfur has also been reported in sulfided

catalysts due to high product water content when applied in high biodiesel, motivating the need to move to sulfur-free or unsulfided catalysts^[161].

Improved hydrodeoxygenation catalysts

New non-conventional hydroprocessing bimetallic catalysts, such as alumina-supported Ni-Fe and Ni-Cu, have been reported as promising HDO catalysts^[148,162]. Ni-Fe/Al₂O₃ was tested on three model compounds of bio-oil: furfuryl alcohol, benzene alcohol, and ethyl oenanthat at 400 °C, and the conversion was found to be 100%, 95.48%, and 97.89%, respectively. The pathway of C-O cleavage was followed^[148]. A synergistic effect of Ni and Cu was attributed to the high HDO efficiency obtained through Cu-Ni/ZrO₂ compared to the monometallic Ni and Cu catalyst^[149]. Although monometallic catalysts show a promising route for HDO, bimetallic and trimetallic catalysts are more promising as they have been shown to inhibit the sintering of the active phase due to their exceptional electronic and dispersion properties^[149]. HDO and decarboxylation products are obtained in the HDO of vegetable oils when using monometallic Mo/SiO₂ and Ni/SiO₂, respectively, while a mixture of decarboxylation and HDO products are obtained through bimetallic Ni Mo/SiO₂ with overall catalytic activity following the order Ni/SiO₂ < Mo/SiO₂ < NiMo/SiO₂^[154]. Similar observations were made in the HDO of rapeseed oil using NiMo/Al₂O₃ > Co/Al₂O₃ > Ni-/Al₂O₃^[154]. Xue *et al.* obtained the highest HDO activity on bioderived phenol through the trimetallic alumina-supported Ni-Cu-Co catalyst when they investigated how the activity varies from monometallic, bimetallic, and trimetallic catalysts using alumina-supported Ni, Ni-Co, and Ni-Cu-Co^[150]. In contrast, Horáček *et al.* found bimetallic NiMo/Al₂O₃ to be more active than trimetallic NiCoMo and NiCoW catalysts^[163].

Numerous HDO catalysts that migrate from traditional alumina supports have been tested. A carbon-supported CoMo catalyst has been studied for the HDO reaction with 4-methyl-acetophenol, guaiacol, and ethyl decanoate as a feedstock below the typical HDO temperature range (280 °C) and 7 MPa^[164]. Successful HDO of phenols in the temperature range of 300-450 °C and 5 MPa using a MgO-supported CoMo catalyst has been reported^[165]. NiW with C support has also been employed for the HDO of phenols at a very low pressure of 1 MPa at a temperature of 250-300 °C, which is lower than the typical HDO temperature range^[166]. Yoosuk *et al.* reported an amorphous unsupported NiMoS catalyst with high HDO activity^[167]. Unsulfided catalysts on neutral supports, such as activated carbon and SiO₂, have also been explored to address the challenges of very low sulfur bio-oils^[155-160].

Noble metals have also been investigated as HDO catalysts, and these are mostly hosted on other supports besides alumina^[168]. Pd/Al₂O₃ was reported to be suitable for the *in-situ* HDO of phenol, *o*-cresol, and *p*-*tert*-butylphenol with high selectivity of cyclohexanone and had better conversions compared to Raney Ni catalysts^[169]. A C/alumina-supported Ru catalyst was tested for the HDO of pyrolysis oil at 350 °C and 20 MPa^[167]. Better hydrocarbon yields have been reported through Pt/Ac catalysts compared to Pt supported on Al₂O₃, Cr₂O₃, and SiO₂^[170]. Wildschut *et al.* tested Ru/C, Pt/C, and Pd/C catalysts and proved that the noble metal catalysts have a higher HDO efficiency compared to alumina-supported NiMo and CoMo catalysts with Ru metal catalysts performing better than Pd and Pt^[171]. A Pt/Al₂O₃ catalyst has been reported for *in-situ* HDO^[55]. Pd supported on activated carbon and Pd nanoparticles were investigated for the HDO of phenol with formic acid under mild conditions, and the study realized that even though the activity of the activated carbon-supported catalysts is better compared to nanoparticles shortcomings included particle aggregation, organic intermediates blocking the active sites, and leaching of Pd^[168]. Table 4 summarizes typical catalysts developed for HDO.

Active and promoter mineral materials in hydrodemetallization catalysts

Conventional hydrodemetallization catalysts

While alkali and alkali earth metal salts in feedstock can be easily removed by washing before distillation,

Table 4. Typical hydrodeoxygenation catalysts

Catalyst	Composition			Feedstock	Reaction conditions	Comments	Ref.
	Active material(s)	Promoter(s)/Additive(s)	Support				
CoMo/Al ₂ O ₃	Sulfided CoMo	-	Al ₂ O ₃	<i>o, m, p</i> -cresols	Autoclave, 360 °C, 7 MPa and 60 min	The efficiency of the HDO reaction of ortho < meta < para. <i>P</i> -cresol reported 95% conversion, while <i>o</i> -cresol had 87% conversion.	[147]
CoMo/Al ₂ O ₃	4% CoO, 15% MoO, 235 m ² ·g ⁻¹ Al ₂ O ₃	-	Al ₂ O ₃	Phenols (methyl substituted)	Microflow reactor, 300 °C, 2.85 MPa	Two pathways were observed DDO (leading to the formation of aromatics) and HYD (formation of cyclohexane).	[9]
NiMo	Unsupported NiMO sulfide	-	-	Phenol	Parr reactor, 350 °C, 2.8 MPa, 60 min, 150 rpm	NiMo sulfide followed HYD pathway, forming aliphatic hydrocarbons with 96.2% conversion due to the addition of Ni, while Mo sulfide followed DDO pathway.	[167]
NiFe/Al ₂ O ₃	15wt.% Ni, 5wt.% Fe	-	Al ₂ O ₃	Furfuryl alcohol, benzene alcohol, and ethyl oenanthane	Tubular reactor, 300-400 °C, atmospheric pressure	A 100%, 95.48%, and 97.89% conversion for furfuryl alcohol, benzene alcohol, and oenanthane was observed, respectively. The byproducts of the reaction include toluene, 2-methylfuran, and heptane. The conversion of oenanthane is more affected by temperature.	[148]
Ni-Cu-Co/Al ₂ O ₃	20Ni-5Cu-5Co/Al, 20Ni/Al, 20Ni-5Cu/Al	-	Al ₂ O ₃	Bio-derived phenol	240 °C, 4 MPa, 6 h	Ni-Cu-Co/Al ₂ O ₃ performs better (100% conversion) than monometallic and bimetallic catalysts (< 80% conversion). The main products of the reaction included cyclohexane and cyclohexanol. Both HDO pathways were illustrated as there was a sign of DDO pathway indicated by the formation of benzene, which is unlikely in situ HDO.	[150]
Cu/Al ₂ O ₃ , Ni/Al ₂ O ₃ , Cu-Ni/Al ₂ O ₃	60wt.% Cu/Al ₂ O ₃ , 60wt.% Ni/Al, 20wt.% Cu-40wt.% Ni/Al	-	Al ₂ O ₃	Furfural	Microbatch reactor, 300 °C, 10 bar/hydrogen donor (methanol/isopropyl)	Bimetallic catalyst Cu-Ni/Al ₂ O ₃ had a better performance when compared to the monometallic analogs of Ni and Cu. Isopropanol is a better hydrogen donor and yields higher conversions compared to methanol.	[149, 162]
Ni/Ce-SBA-15	5wt.% Nickel	Cerium 0.08 Ce:Si ratio	Ce-SBA-15 696 m ² /g, 0.98 cm ³ /g, pore diameter 9.3 nm	4wt.% anisole in heptane	Fixed-bed tubular reactor, 200 mg catalyst in SiC, 7 bar, 290 °C	Improved catalytic activity and selectivity towards benzene (double compared to Ni/SBA-15). Ce promotion is more efficient for intermediate Ce content Ce/Si = 0.03. Better performance is also attributed to better dispersion of the metallic phase and formation of specific active sites in the Ni particles in contact with Ce-containing surface species.	[172]
Pd/Al ₂ O ₃ vs. Raney Ni	3wt.% Pd, Raney Ni: 9:11 (Ni:Al)	-	Pd/Al ₂ O ₃ : 250 m ² ·g ⁻¹ of Al ₂ O ₃ , 80-120 mesh	Phenol, <i>o</i> -cresol, <i>p</i> - <i>tert</i> -butylphenol	Tubular reactor, 470-490 K, 3.5 MPa	Phenol HDO Pd/Al ₂ O ₃ cyclohexanone selectivity: 96.1%, 92.4%, and 71.1%, with methanol, ethanol, and H ₂ as hydrogen sources, respectively. HDO of phenol Raney Ni cyclohexanone selectivity: 20.5%, 27.4%, and 12.6%, with methanol, ethanol, and H ₂ as hydrogen sources, respectively. Conversions using Pd/Al ₂ O ₃ : H ₂ > EtOH > MeOH, phenol (82.5%) > <i>o</i> -cresol > <i>p</i> - <i>tert</i> -butylphenol (0.65%). Better HDO of <i>o</i> -cresol with EtOH as hydrogen donor as compared to Raney Ni.	[169]
Ru/C, Ru/TiO ₂ , Ru/Al ₂ O ₃ , Pt/C, Pd/C	5wt.% of active metal	-	C	Bio-oil	Batch autoclave, two-stage operating conditions: 250 and 350 °C, 100 and 200 bar, 4 h	Ru/C showed a higher yield of 60wt.% and had better HDO performance (90wt.%) than other noble metal catalysts. Ru/C yields better-upgraded oil than traditional CoMo/Al ₂ O ₃ . Pd/C had higher yields than Ru/C, but oil had a high oxygen content.	[171]
Pt/Al ₂ O ₃ , Pt/TiO ₂	-	-	Al ₂ O ₃ , TiO ₂ , ZrO ₂ , SiO ₂	Bio-oil	Autoclave, 350 °C, 6.9 bar	Pt/Al ₂ O ₃ showed better performance compared to other Pt catalysts, reducing oxygen content from 41.4wt.% to 2.8wt.%. Supports influence	[55]

Pt/ZrO₂,
Pt/SiO₂-
Al₂O₃SiO₂-Al₂O₃

how well the catalyst performs in HDO

DDO: Direct deoxygenation; HDO: hydrodeoxygenation; HYD: hydrogenation.

heavy metals can only be effectively removed through HDM using catalysts and hydrogen at high temperatures^[7,173]. Conventional alumina-supported NiMo, CoMo, and NiW hydrotreating catalysts have been reported for HDM^[173,174]. Nickel removal from bitumen-derived and Conradson carbon residue oils was investigated using a commercial NiMo/Al₂O₃ catalyst; high Ni removal was achieved under mild conditions^[175]. Ancheyta-Juárez *et al.* studied the HDM of Maya heavy crude using Ni-Mo/Al₂O₃ catalysts, cited diffusion limitation to the effective processing of large molecules, and recommended high catalyst pore volumes in the range 100-250 Å to be optimal for HDM^[176]. Similar pore size ranges were also reported by Liu *et al.* when they tested Ni-Mo/Al₂O₃ catalysts on the HDM of Saudi Arabia vacuum residuum^[177]. They indicated high HDM activity for the smaller and middle range Ni and V compounds, but effective HDM of the larger compounds required macropores (> 100 Å)^[177]. HDM is easy, but the deposition of metal products is a challenge that necessitates considerations for catalyst metal retention capacity, pore structures, size distributions, and acid-base properties of the support and catalyst morphology^[7,178]. Organometallic compounds of high molecular weight and dimensions that approach or exceed catalyst pore size also cause fouling of catalysts^[179-181]. Metals cause or promote catalyst deactivation as they accumulate on catalyst surfaces through deposition (e.g., as metal sulfides)^[181,182]. Fe bound by naphthenates causes plugging when it forms FeS in catalyst beds and filters. FeS also enhances coking reactions^[7]. Catalyst activity, selectivity for desired products, and lifespan are influenced. Heavy metals also restrict conditions for the disposal of spent catalysts^[181]. Heavy metals are commonly found in porphyrin rings and are mostly concentrated in high boiling point fractions (e.g., heavy oil residues, asphaltenes, and resins), with V and Ni being the most abundant in most oils^[7,178,181]. These aspects motivate the continuous development of HDM catalysts, especially since HDM is important as a first step to protect downstream catalysts for cracking, HDS, HDN, and HAD^[7,173,174].

Improved hydrodemetallization catalysts

Alumina-supported HDM catalysts are not efficient as they suffer deactivation through the deposition of metals on active sites and pore plugging arising from accumulations of metal sulfides^[180]. Rana *et al.* used carbon as a support for HDN and observed that carbon support leads to weak metal support interaction, resulting in more Type II active sites that increase the deposition of metal on the carbon surface, preventing overlaying on existing MoS₂ sites^[178]. Rana *et al.* also investigated the incorporation of TiO₂ into alumina to produce a CoMo/TiO₂-Al₂O₃ and obtained better textural properties and higher HDS activity but a lower HDM activity, indicating the need for higher average pore diameter and macropore size distribution to achieve higher HDM activity^[183]. Rana *et al.* attributed much of the HDM catalysis activity to Mo sites when they tested the promoter effect of Fe, Co, and Ni, observing the trend of Fe > Co > Ni for the promoters^[178]. They also investigated the effect of mixing peptized alumina with activated carbon to reduce diffusion limitations of larger compounds such as asphaltenes and enhance the metal storage capacity of the catalysts. Patents are also available for Mo, W, and Fe (with Co, Ni, or Fe promoters) and 1:1 alumina to carbon extrudate support with a bimodal type pore size distribution (i.e., both meso- and macro-porosity), and a magnesium aluminosilicate clay as potential HDM catalysts^[184,185]. Typical catalysts that have been developed for HDM are summarized in [Table 5](#).

Table 5. Typical hydrodemetallization catalysts

Catalyst	Composition			Feedstock	Reaction conditions	Comments	Ref.
	Active material(s)	Promoter(s)/Additive(s)	Support				
Commercial NiMo/Al ₂ O ₃	Mo	Ni	Al ₂ O ₃	bitumen-derived heavy oils and Conradson carbon residue	625-685 K, LHSV = 0.14-0.80 h ⁻¹ , 13.7 MPa, H ₂ /oil ratio = 890 m ³ .m ⁻³	High Ni removal under mild conditions with minor improvements with increasing severity of conditions.	[175]
Ni-Mo/Al ₂ O ₃	Mo	Ni	Al ₂ O ₃	Vacuum residue	410 °C, LHSV = 0.3 h ⁻¹ , 15 MPa, H ₂ to liquid was 600	The percentage of light impurities easier to remove on spherical catalysts (78.20% and 39.43% in HDM and HDCCR reactions, respectively) is higher than 65.20% and 17.50% on cylindrical catalysts.	[186]
Commercial NiMo/Al ₂ O ₃ (B), and NiMo/Al ₂ O ₃ (A) {has high metal content}	Mo	Ni	Al ₂ O ₃	VO-TPP in o-xylene, thiophene	600 K, LHSV = 0.2 h ⁻¹ , 8.0 MPa	The model results showed that the pore blocking rate in catalyst B was lower than in catalyst A. These data confirm that it is a durable high-performance HDM catalyst.	[187]
Co-Mo/γ Al ₂ O ₃	Mo	Co	γ Al ₂ O ₃	Asphaltenes, diesel, extra heavy oil	360-410 °C, LHSV = 1.0 h ⁻¹ , 4.0 MPa, H ₂ /oil ratio = 600 nL.L ⁻¹	The catalyst synthesized on a carrier with cylindrical pores exhibited higher catalytic activity in sulfur, heavy metals, and asphaltenes removal reactions that are synthesized on a carrier with slit-like pores.	[188]
FeMo, CoMo, NiMo	Mo	Fe, Co, Ni	(0%-75% activated carbon in alumina	residual oil and heavy crude oil (Ku crude)	380-400 °C, LHSV = 1.0 h ⁻¹ , 120 bar, H ₂ /Oil = 680	Carbon in support reduced coke and metal depositions on pore-mouth and catalytic sites. The optimum textural and mechanical properties of the support are obtained at a 1:1 carbon-alumina weight ratio. FeMo-supported catalyst composition (10wt.-%-75wt.-% carbon) had the best HDM results for an optimum pore diameter.	[178]

HDCCR: Hydrodemetallization and continuous catalyst regeneration; HDM: hydrodemetallization; LHSV: liquid hourly space velocity; VO-TPP: vanadium oxide tetraphenyl porphyrin.

Active and promoter mineral materials in hydrocracking catalysts

Conventional hydrocracking catalysts

There are two extreme hydrocracking catalytic functions: an acidic functionality and a hydrogenation/dehydrogenation functionality^[189]. The acidic functionality constitutes bond cleavages, isomerizations, and intermolecular and intramolecular skeletal rearrangements, including cyclizations. The acidic functionality is provided by support materials such as silica-alumina, zeolites, or alumina^[9,179,190]. Cracking reactions usually require protonic (Brønsted) acid sites^[179,190]. The hydrogenation/dehydrogenation functionality has a hydrogenolysis character that cleaves bonds of reactants into fragments, dehydrogenates saturated reactants to produce reactive olefin intermediates, hydrogenates the unsaturated products from cracking, and prevents catalyst deactivation by hydrogenating coke precursors. These two extremes result in different product distributions. The extent of each of these reactions varies from catalyst to catalyst. Hydrocracking catalysts of commercial importance possess dual functionality, with reactions being primarily catalyzed by a strong acidic functionality and a weak hydrogenation/dehydrogenation functionality with minimal hydrogenolysis.

Conventional sulfided hydrotreating catalysts, such as CoMo/Al₂O₃ and NiMo/Al₂O₃, do not have sufficient protonic acidity to afford good cracking functionality even at high temperatures (400 °C)^[179,190]. However, feed pre-treatment using these catalysts is essential to reduce the heteroatomic impurities since hydrocracking catalysts are sensitive to inhibition and/or poisoning^[9,191,192]. This pre-treatment also helps with saturation of olefins and aromatics. One of the early successful hydrocracking catalysts was pelleted WS₂^[193]. There is also a wide body of literature on hydrocracking tests using traditional hydrotreating NiMo, CoMo, and NiW catalysts^[194]. Hydrocracking of poly-aromatic hydrocarbons to mono-aromatic hydrocarbons has been reported using NiMo/Al₂O₃-HY and NiMo/Beta catalysts^[195]. The use of CoO-MoO₃/Al₂O₃ for hydrocracking of heavy feedstock is common, and promotion of the catalyst with Na, K, or Li has been reported, with Li showing the best results^[194].

Improved hydrocracking catalysts

Improved hydrocracking through modified conventional hydrotreating catalysts has been reported^[89,196,197]. A Ni (1wt.%, 2wt.%, and 3wt.%) modified sulfated zirconia (SO₄/ZrO₂) catalyst was investigated for hydrocracking activity and selectivity, and the catalyst loaded with 1% Ni had the highest acidity producing the highest activity and selectively for the gasoline range (70.28%)^[198]. Bimetallic catalysts have been reported to show better activity^[77,199]. Bimetallic CoWS₂ catalysts were found to have higher hydrocracking activity compared to monometallic Co₉S₈ and WS₂ catalysts^[199]. Bimetallic Ni-W catalysts showed high catalytic activity (78%-91% conversion) compared to monometallic Ni catalysts (74.2%-82.7% conversion)^[77]. Hydrocracking of waste plastic pyrolysis oil and vacuum gas oil using a NiW/HY catalyst and plastic pyrolysis oils using a Ni/SBA-15 have been reported^[200]. Catalysts constituting multiple metals to fine-tune the bifunctionality have also been reported. Liu *et al.* carried out hydroconversion of polyolefins using Pt/WO₃/ZrO₂ and HY zeolites and reported an 85% yield at 225 °C^[201]. Pt had the role of activating the polymer followed by cracking on WO₃, ZrO₂, and HY zeolites, which are acid functions ending. WO₃ and ZrO₂ sites were responsible for isomerization, and Pt was responsible for hydrogenation of the olefin intermediates. There is a special category of hydrocracking catalysts called shape-selective catalysts that utilize crystalline aluminosilicates with pore structures of specific geometrical characteristics that restrict access of reactants and products to particular sizes and shapes^[189]. A novel class of promising hydrocracking catalysts based on stable single-atom Mo has recently been reported by Sun *et al.*^[202]. Good hydrogenation activity, high liquid oil yields, and reduced tendency of coke formation were observed when tested on slurry phase hydrocracking of vacuum residue.

For the hydrogenation/dehydrogenation functionality, metals from Group VIII and VIb are selected based on their hydrogenation capabilities, and noble metals, such as Pt, Pd, and Pt/Re, and transition metals, such as nickel, cobalt, molybdenum, and tungsten, have been reported to be among the best performers^[9,67,189]. Pt and Pd have good hydrogenating functions but must be used in an environment that does not have sulfides^[203]. Higher hydrogenation and less cracking activity by Pt compared to NiMoS-supported bifunctional catalysts were observed by Brito *et al.* during the hydrocracking of octylcyclohexane^[203]. The use of chromium, niobium, and Sn has also been reported but not as extensive^[9,67]. Nanoparticles of noble metals and transition metal oxides, nitrides, and carbides have also been reported for the hydrogenation component of hydrocracking catalysts^[204,205]. Typical catalysts developed for hydrocracking are presented in Table 6.

SUMMARY AND PERSPECTIVES

Conventional hydroprocessing catalysts [Co(Ni)Mo/Al₂O₃ and Ni(Mo)W/Al₂O₃] have met the hydroprocessing industry catalyst needs, but better hydroprocessing catalysts are now being highly sought after to meet the increasing demand for petroleum products, achieve stricter fuel specifications, and selectively target individual hydroprocessing reactions to accommodate unique feedstocks and/or obtain

Table 6. Typical hydrocracking catalysts

Catalyst	Composition			Feedstock	Reaction conditions	Comments	Ref.
	Active material(s)	Promoter(s)/Additive(s)	Support				
NiMo/Al ₂ O ₃ -HY and NiMo/Beta	Mo (and 15wt.% MoO ₃)	Ni (5wt.% NiO)	Al ₂ O ₃ -HY and Beta	Tetralin or 1-MN	Fixed-bed reactor, 320-420 °C, 6 MPa WHSV = 2 h ⁻¹	NiMo/Beta(25) possessed high Brønsted acidity and high MoS ₂ dispersion and can facilitate the conversion of intermediates of 1-MN hydrocracking (mainly methyl tetralins and indanes) into MAHs. NiMo/A ₃₀ Y ₅₀ - NiMo/Beta(25) (up to 99.9% conversion of 1-MN and 63.8% selectivity of MAHs). NiMo/A ₃₀ Y ₅₀ with 30wt.% Al ₂ O ₃ showed the best performance in selective hydrocracking reactions owing to the high density of MoS ₂ and BAS.	[196]
NiMo/γAl ₂ O ₃ , NiMo/γAl ₂ O ₃ + Beta	Mo	Ni	γAl ₂ O ₃ and γAl ₂ O ₃ + Beta	Naphthalene	Fixed bed reactor, 400 °C, 4 MPa	Catalytic performance is dependent on the coupled hydrogenation ability of NiMo/γ-Al ₂ O ₃ and the acidity of Beta zeolite. The highest BTX selectivity (62.8%) at 98% naphthalene conversion in Ni(2)Mo(13.2)/γ-Al ₂ O ₃ + Beta(20) due to well-matched HYD and acid function.	[197]
NiMo/REY + Al ₂ O ₃	Mo	Ni	REY + Al ₂ O ₃	Vacuum gas oil	Fixed bed reactor, 390 and 410 °C, 16.0 MPa, LHSV = 0.7 h ⁻¹	A high yield of middle distillates fraction (50.5wt.% at 410 °C) was achieved. Increase in selectivity to middle distillates selectivity can be explained by a decrease in the strong acid site density that suppresses overcracking reactions to produce naphtha.	[89]
NiW/Y-ASA-Al ₂ O ₃	W	Ni	Y-ASA-Al ₂ O ₃	Straight-run gas oil, dimethyl disulfide, and aniline, vacuum gas oil, unconverted oil	Fixed bed reactor, 340-410 °C, 16.0 MPa, LHSV = 1.4 h ⁻¹	Increase of zeolite content in the catalysts leads to an increase of activity and a decrease of selectivity to diesel in second-stage hydrocracking. Increased activity is attributed to the increasing BASs.	[198]
CoWS ₂	W	Co	-	Vacuum residue	Autoclave batch reactor, 693 K, 10 MPa	Bimetallic CoWS ₂ catalysts have higher activity than monometallic Co ₉ S ₈ and WS ₂ catalysts in regard to hydrocracking TOF and C7-ASP conversion for vacuum residue hydrocracking. CoWS ₂ has well-dispersed mono-slabs with a better dispersion of 11.1 nm and stability.	[199]
Ni/Zeolite-Y, Ni-W/Zeolite-Y and NiW/HY	W (22.7wt.% WO ₃)	Ni (4.54wt.% NiO)	Zeolite-Y and HY	Heptane	Batch reactor, 400-440 °C, 80 bar	Higher catalytic activity (conversion, 78%-91%) Ni-W catalysts than Ni-based monometallic catalysts (conversion, 74.2%-82.7%), with NiO-WO ₃ -ZY30(SiO ₂ /Al ₂ O ₃ ratio equal to 30) exhibiting the highest conversion.	[77]
Pd/x (where x = SBA-15, ASA, MCM-41, and MCM-48)	1wt.% Pd	-	SBA-15, ASA, MCM-41, and MCM-48)	n-hexadecane	Packed bed, 473 K, 60 bar WHSV = 10 g _{n-C16} ·g _{cat} ⁻¹ ·h ⁻¹	All materials (including ASA) exhibited low acidity compared to zeolites. Increasing Al content reduced the order of mesopores. Ideal hydrocracking operation is approached for ASA, MCM-48, and SBA-15 prepared at high pH contained disordered mesopores.	[59]

HYD: Hydrogenation; LHSV: liquid hourly space velocity; TOF: turnover frequency; WHSV: weight hourly space velocity; 1-MN: 1-methylnaphthalene.

specific products^[206,207]. For example, selective coordination and saturation of N-heteroaromatics are important to minimize saturation of unsubstituted aromatics and the need for additional reforming steps to achieve high-octane fuel^[119]. There is an increasing need to accommodate feedstocks, such as sour and heavy crudes, bio-oils, waste plastic, biomass, and coal pyrolysis oils, to meet the increasing demand for petroleum products and as alternative sustainable sources, especially biomass and bio-oils. These products come with heavier concentrations of heteroatomic compounds, especially the refractory compounds^[7]. They require hydrocracking, yet hydrocracking catalysts are vulnerable to inhibition and poisoning by heteroatoms^[207-210]. Considerations for

catalyst deactivation (poisoning by intermediates or products, sintering of support materials or metallic components) and coke deposition need to be made when designing catalysts and choosing operating conditions for these feedstocks^[9,209-213]. For example, specific catalysts need to be designed for processing feeds with large concentrations of oxygen-containing compounds since higher amounts of water are produced, which leads to dealumination of alumina supports, and HDO being a highly exothermic process also means increased HDO of higher oxygen content feeds can result in heat build-up in reactors^[9,119,211].

The periodic trends for the active metals are well understood, and the high catalytic activities and selectivities of noble metals are not contested. Noble metals are required in small quantities. High HDN activity and HDN/HDS selectivity were obtained through 1% Ir supported on various materials compared to the conventional NiMo system^[214]. Nevertheless, the relative abundance of noble metals in the Earth's crust is too low to meet current needs; they are expensive and sensitive to sulfur poisoning^[215]. Solutions to increasing the resistance of noble metals to poisoning by sulfur have been explored^[52]. They are usually employed as second-stage catalysts in pre-treated feeds that have reduced sulfur^[38]. They are useful in shaping the finer properties of oils, e.g., deep desulfurization and hydrogenation. The relative abundance of the non-noble metals that are most active is also much lower than that of the less active ones. Although Mo and W lie in the sweet spot, their abundance is also low and cannot be projected to meet the increasing demand^[37,107]. The drive to use other metals, such as Nb, V, and Fe, recently attracted extensive attention, especially iron (Fe). Fe is one of the metals of interest to be considered for substituting the conventionally used catalysts due to its high crust abundance, low cost, and environmental non-toxicity^[37,107]. A synergistic effect between Fe and Mo, Ni, or V has been studied for HDS^[207]. Although it has been widely considered that the Fe-based catalysts exhibit poor HDS performance, the addition of Zn was found to significantly enhance HDS activity^[216]. The promotional effect of Zn comes from the formation of an active FeZnS phase that triggers a strong electron-donating effect from Zn to Fe species and the generation of more sulfur vacancies that change the electronic state of Fe^[37,63]. Sudhakar *et al.* patented Fe-Mo sulfide catalysts that are as highly active for HDN as they are for HDS^[22]. HDO using Ni-Fe and Ni-Cu has been reported^[148,162].

Several efforts are also being made to migrate from traditional sulfides. Various transition metal carbides, nitrides, phosphides, borides, hydrides, oxycarbides, and oxynitrides have been notably tested to modulate the characters of transition metals and obtain noble metal-like properties and even obtain bifunctionality in processes such as hydrocracking^[93]. Good HDS and HDN activities have been reported through transition metal carbides^[15]. Ternary catalysts for HDS, HDO, HDN, and HDC have also been explored^[97]. The metal ratios in the ternary catalysts were found to be important for the concentrations of active phases, dispersion of active phases, and the textural characteristics that influence accessibility of reactive surfaces^[121].

Aside from the active metal phase, the catalytic support also has a great influence on the performance of hydroprocessing catalysts^[37,63]. The role played by supports is now understood, and modification of supports is now considered a crucial component to achieving high catalyst activity and selectivity. Alumina supports are the most prominent in hydroprocessing catalysts. Their functionality in certain processes is limited due to their strong interaction with the active metals, which impedes sulfidation, resulting in poor catalytic activity. The strong acid sites also promote undesirable reactions that lead to higher coke formation and catalyst deactivation^[51,217]. There are various reports on modification of the alumina supports to control the acidity, completely migrating to other support materials such as zeolites or making composite materials to benefit from the attractive properties of multiple support materials^[36,76]. For example, chelating agents are used to cover the surface of Al₂O₃ with a carbon layer to reduce the metal support interaction and improve resistance to deactivation by coke deposition. Al₂O₃-carbon composites combine the positive characteristics of the individual components to give optimum support. Mendes *et al.* investigated a Ni₂P catalyst supported

by an Al_2O_3 -carbon composite and reported reduced interactions of phosphorus with alumina and minimal formation of inactive P deficient phases, Ni_{12}P_5 and AlPO_4 ^[215]. The biggest challenge observed when making support material composites was the difficulty in controlling the composition and distribution of mesopores and micropores, which, in turn, affects accessibility and effective promotion of the active metals. The methods used for support preparation are also crucial to get the right catalyst properties such as optimum acidic nature, selectivity, optimal metal-support interaction, and textural properties^[35]. The effect of impurities in catalysts also needs to be taken into consideration, and the choice of starting material can be of importance in that regard, as observed in a study where the influence of the Ir precursor: $[\text{Ir}(\text{AcAc})_3]$, $\text{Ir}_4(\text{CO})_{12}$, H_2IrCl_6 , $(\text{NH}_4)_2\text{IrCl}_6$] in obtaining alumina-supported 1% Ir catalysts was investigated and $\text{Ir}_4(\text{CO})_{12}$ was found to provide a catalyst with the highest activity owing to less impurities rather than better dispersion of Ir in the catalyst^[214].

Overall, multiple factors work in synergy to provide the optimum catalyst performance with suitable properties that allow for a long catalyst lifespan. A balance needs to be struck depending on the feedstocks or expected products.

CONCLUSIONS AND OUTLOOKS

Heterogeneous hydroprocessing catalysis relies on various mineral materials. Wide strides have been made in improving the catalysts following a better understanding of the interactions between the various mineral materials used as supports, active metals, promoters, additives, *etc.* The attractive properties of noble metals (e.g., high activities and selectivities) are identified throughout all the processes discussed in contrast to their vulnerability to poisoning under hydroprocessing conditions (e.g., where sulfur is present) and the fact that they are expensive and found in small quantities. Catalysts with properties that resemble those of noble metal catalysts have been obtained through well-thought combinations of cheaper mineral materials (active and promoter metals and supports), using suitable precursor mineral materials, and understanding synthesis protocols and modifications. Perfecting the catalytic properties using abundant metals such as iron will ensure sustainability, benefitting the hydroprocessing industry and environment in many regards. Better catalysts will also enable the utilization of unconventional feedstocks to meet the increasing demand for particular petroleum products. The review shows that there is a large pool of literature to be repurposed to advance commercialization of technologies involving unconventional feedstocks such as pyrolysis oils, bitumen, and shale-derived oils.

DECLARATIONS

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