ABSTRACT The increasing energy demand is building an impetus for extraction of liquid fuels from oil sands. This chapter describes the process of extraction of liquid transportation fuels from oil sands. The hydrocarbon mixture called bitumen is extracted from oil sands mainly via surface mining. For deep bituminous reserves, the steam-assisted gravity drainage (SAGD) technique is used. The bitumen is separated from sand, clay, or other minerals and water via a series of processes described in this chapter. It is upgraded by fractionation in atmospheric and vacuum distillation units. The long-chain carbon molecules are broken into smaller value-added molecules in hydrocracker and coker units, and the excess carbon is removed in the form of coke in the coker unit. The main product streams from the primary upgrading include naphtha, light gas oil (LGO), and heavy gas oil (HGO). The sulfur and nitrogen content present in the bitumen is transmitted to HGO and LGO. HGO contains 3.5–4.5 wt.% sulfur and 0.35–0.45 wt.% nitrogen, whereas LGO contains 2.0–2.5 wt.% sulfur and 0.12–0.17 wt.% nitrogen. These impurities need to be removed by the hydrotreating process before transferring the HGO and LGO for downstream refining in order to obtain the product specifications of liquid transportation fuel. Hydrotreating is a catalytic process, and a thorough understanding of the catalyst is required to develop a highly efficient catalyst. The better the catalytic performance, the better is liquid fuel quality and process economics. This chapter discusses about various hydrotreating NiMo catalysts supported on a variety of mesoporous materials including SBA15, M-SBA15 (M = Al, Ti, Zr); mesoporous ZrO$_2$ and Al$_2$O$_3$; and mesoporous mixed metal oxide TiO$_2$–Al$_2$O$_3$, ZrO$_2$–Al$_2$O$_3$, and SnO$_2$–Al$_2$O$_3$. The reaction mechanisms and the role of the catalyst are explained by a thorough characterization of catalysts using X-ray diffraction (XRD), N$_2$ adsorption–desorption isotherms, Fourier transform infrared spectroscopy (FTIR), X-ray absorption near-edge structure (XANES), and high-resolution transmission electron microscopy (HRTEM). The hydrotreated LGO, HGO,
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and naphtha are blended to make synthetic crude, which is then processed in the existing refineries to obtain high-quality liquid fuels such as diesel, gasoline, kerosene, jet fuel, and petrochemicals. However, this industry faces many challenges, including bigger environmental footprint, tailing ponds, water usage, technological limitations, coke management, and land reclamation.

5.1 Introduction

The worldwide increasing development and flourishing economy needs more energy. Petroleum being the available major source of energy is being exploited to meet the high energy demand. The global oil consumption in 2015 was around 94 million barrels per day (mb/d), and its growth is expected to increase by 1.2 mb/d in 2016 (Oil Market Report 2015; Yardeni and Johnson 2015). To comply with this huge demand for oil, both conventional and nonconventional resources are exploited. The conventional resources are those that provide crude oil by drilling the well and the oil flows out of the reservoir. However, oil extraction from unconventional resources requires specialized techniques because the oil trapped in reservoirs have high viscosity and little or no ability to flow. This includes oil sands, oil shale, coal, and biomass-based liquid supplies, and Venezuelan extra-heavy oil and natural bitumen.

Oil sands are the major source of unconventional oil, and Canada is the world’s largest commercial producer of crude oil from oil sands. Canada has 174 billion barrels of oil, of which 169 billion barrels are oil sands reserves. The total oil sands-derived oil production in 2014 reached about 2.3 mb/d (Upgraders and Refineries Facts and Stats 2015). Oil sands are a mixture of sand, clay or other minerals, water, and bitumen. The bitumen is a dense and viscous hydrocarbon mixture from which crude oil is extracted. It is as viscous as cold molasses at room temperature. The National Energy Board of Canada defines bitumen as “a highly viscous mixture of hydrocarbons heavier than pentanes which, in its natural state, is not usually recoverable at a commercial rate through a well because it is too thick to flow.” The World Energy Council defines natural bitumen as “oil having a viscosity greater than 10,000 centipoise under reservoir conditions and an API gravity of less than 10° API.”

Majorly, the bitumen is extracted via two techniques: surface mining and steam-assisted gravity drainage (SAGD). The latter is used in places where bituminous deposits are too deep to be mined. For surface mining, large trucks and shovels are used, and the oil sand is transported via big trucks to the extraction facility. It is then crushed and conveyed to the rotary drums (see Figure 5.1). In the rotary drum, hot water and chemical agent (caustic) are added. The hot water reduces the viscosity of bitumen and makes it flow. The water, sand, and bitumen mixture is then transferred to the gravity settler/seperator. The bitumen froth being lighter stays on the top, and the water, sand, and chemical mixture in the bottom of the separator is sent to the tailing ponds for treatment. The bitumen froth is treated with hydrocarbon solvent (naphtha, hexanes) in the froth treatment unit, and the extracted bitumen is sent for upgrading (Sustainable Development of Oil Sands-Challenges in Recovery and Use 2006; The Oil Sand Extraction Process 2008; Diagram of Oil Sands Mining and Extraction 2016; Sensors for Mining and Bitumen Extraction 2016). The extraction of bitumen from oil sands using the hot water drum process is a big component of oil extraction, and bitumen recovery determines the economics of the entire oil sands to liquid fuels process. Masliyah et al. (2004) have discussed in detail the water-based extraction of bitumen from oil sands in their review paper.
In the SAGD process, a high-pressure steam is injected into the underground formation as shown in Figure 5.2. The high temperature of the steam makes bitumen to flow, and it is pumped out of the surface and sent for upgrading (Talk about SAGD 2013; Chahal et al. 2015).

**FIGURE 5.1**

**FIGURE 5.2**
5.2 Bitumen Upgrading

Bitumen is a complex hydrocarbon mixture and highly viscous with an American Petroleum Institute (API) gravity of around 8.5. It contains 4–6 wt.% sulfur and about 0.3–0.6 wt.% nitrogen. In order to extract the usable crude oil from bitumen and process it in the existing refineries along with conventional crude oil, bitumen upgrading is required. The upgrading process is divided into two stages: primary upgrading and secondary upgrading. Primary upgrading includes the distillation of bitumen to obtain different boiling range cuts, whereas secondary upgrading includes the enrichment of product quality by removing the impurities such as sulfur, nitrogen, and metals.

5.2.1 Primary Upgrading

In this process, the distillates, including naphtha, kerosene, light gas oil (LGO), and heavy gas oil (HGO), were extracted from the bitumen in a series of operations such as atmospheric distillation, vacuum distillation, hydrocracking, and coker (see Figure 5.3).

5.2.1.1 Atmospheric Distillation Unit

The diluted bitumen (with naphtha) is sent to the atmospheric distillation unit (ADU) after preheating at 350°C (see Figure 5.3) to recover the naphtha and to extract the volatiles and LGO with nondestructive distillation. A temperature higher than 350°C results in thermal cracking of feedstock. This may cause the coke formation, and the coke deposits can cause the failure of distillation unit. Generally, The ADU contains 30–50 fractionation trays with high temperature at the bottom and low temperature at the top of the unit. The portion of the condensate from the top of the tower is sent back as reflux that helps in fractionation. The products are withdrawn from the side streams. Typically, naphtha has a boiling range of C₅ to 177°C so it is withdrawn from the upper section of the unit. The LGO, which

![FIGURE 5.3](primary://localhost/10.3.97.143/10 Aug 2023/9781315153292-5/chapter5/5.2.1-AADU.png)

Primary upgrading of bitumen.
is in the boiling range of $177^\circ C$–$343^\circ C$ (Product Specification 2015), is collected from the middle lower section of the ADU. As the product side stream is in equilibrium with the vapor phase, some of the lighter ends are also withdrawn. Therefore, the side stream product is stripped for removing unwanted volatiles in a separate tower containing 4–10 trays (Gray et al. 2007). A fractionation tower (ADU) may be 13 feet in diameter and 85 feet high; however, the side stream stripper tower may be 3–4 feet in diameter and 10 feet high (Ancheyta and Speight 2007). The bottoms from the ADU called as topped bitumen are mainly sent to the vacuum distillation unit (VDU).

### 5.2.1.2 Vacuum Distillation Unit

Vacuum distillation is used to recover the high boiling fraction from the topped bitumen without using thermal decomposition. Typically, the VDU operates at 10–40 mmHg pressure, and the temperature is limited to $350^\circ C$–$380^\circ C$ (further higher temperatures result in cracking of the topped bitumen). The vacuum of 10–40 mmHg pressure is typically maintained by a three-stage steam ejector system. The boiling point decreases under vacuum and this causes a significant increase in the volume of the vapor. Therefore, the VDU is designed with large diameters to maintain the comparable vapor velocities. It may have a diameter of 40 feet or more (Gray et al. 2007). The internal of VDU is different from ADU. The vacuum distillation column internals consist of both trays and packing. To maintain the lower pressure drop, a packing material (such as Raschig rings or structural sheet metal) is used to facilitate the vapor liquid contact. However, the distillations trays are often used at the location of product withdrawals from the side of column. LGO is collected from the top section of the VDU and HGO is collected from the middle section of the VDU (Xu et al. 2005). HGO has a boiling range of 343$^\circ C$; however, it may be obtained at 250–350$^\circ C$ under vacuum. The bottom from the VDU is called as residuum and is sent to the coker and hydrocracker for further upgrading.

### 5.2.1.3 Hydrocracker Unit

The extraction of low-boiling, high-valuable products (naphtha and gas oils) from high-boiling (>500$^\circ C$) residues of the ADU and VDU can be achieved by hydrocracking. This helps in getting more valuable products from the barrel. In the hydrocracker unit, the long-chain heavy hydrocarbon molecules present in the topped bitumen and residuum are broken down into smaller valuable molecules but in the presence of catalyst and hydrogen. The catalyst helps in cracking the long-chain molecules, and the hydrogen saturates these molecules. Therefore, in comparison with cokers, hydrocrackers produce high-quality liquid fuels having an improved hydrogen/carbon (H/C) ratio. Hydrogenation is an exothermic process, whereas cracking is an endothermic process. The resultant heat released is quenched by passing hydrogen at multiple locations in the hydrocrackers. The hydrocracked feed is then sent to the fractionator to obtain HGO, LGO, kerosene, and naphtha. The hydrocrackers typically operate at high pressures (100–150 bar) and high temperatures ($400^\circ C$–$430^\circ C$) (Sahu et al. 2015). The conventional catalysts used for hydrocracking are bifunctional acid and metal sites. Acid sites help in cracking, whereas metal sites favor hydrogenation. Typically, the hydrocracking catalyst comprises a silica–alumina (zeolite)-based support material, which provides cracking sites, and metals such as platinum, palladium, tungsten, and nickel, which supports hydrogenation (Gray et al. 2007). There are mainly two types of hydrocrackers used for upgrading the residue from VDU (boiling point > $550^\circ C$) and ADU (boiling point > $350^\circ C$): fixed bed and
ebullated bed. In fixed-bed reactors, the catalyst is packed in the bed, and after the catalytic deactivation due to coking and fouling, the reactor is shut down to remove the catalyst. The regenerated/fresh catalyst is loaded again in the reactor. However, in ebullated bed reactors such as LC-finer, the catalyst is in suspension or expanded with liquid and gas phases (just like fluidized-bed reactor). The feed and \( \text{H}_2 \) are pumped from the bottom of the reactor, and the effluent/products are withdrawn from the top of the reactor. The products are separated to remove undesirable gases such as \( \text{H}_2 \text{S} \) and \( \text{NH}_3 \), and the liquid is sent for fractionation. The spent catalyst is continuously taken out and the regenerated catalyst is fed back to the reactor. The LC-finer hydrocracker unit operates for long periods of operations without shutdown (3+ years), provides the most efficient heat recovery, and achieves the maximum conversion to light clean products. Typical yields from the LC-finer unit are 17 wt.% naphtha, 10 wt.% kerosene, 19 wt.% LGO, and 37 wt.% HGO (Gray et al. 2007). The bottoms of the hydrocracker unit are sent to the cokers.

### 5.2.1.4 Coker Unit

The residuum (from the VDU) and some of the topped bitumen (from the ADU) are sent to the coker unit to remove excess carbon content. This results in increasing the H/C ratio of the gas oils derived from this unit and hence helps in generation of higher value products from high-molecular-weight, low-value residuum. The excess carbon is removed in the form of solid residue known as petroleum coke. The high temperature in the coker (480°C–550°C) helps in thermal cracking of long-chain bitumen molecules into more valuable short-chain molecules such as kerosene (boiling range 143°C–260°C), LGO, HGO, and naphtha. A typical coking unit consists of a reactor, where a high temperature of 480°C–550°C is maintained to facilitate the thermal cracking reaction (Gray 1994), and the cracked products (liquid and vapors) are transferred to the fractionation column to attain different fractions of products based on the boiling point (Gray et al. 2007). This primarily includes naphtha, kerosene, coker light, and HGO as shown in Figure 5.3.

There are mainly three types of coker units: delayed coker, fluid coker, and flexicoker. In the delayed coking process, the feed is preheated to a cracking temperature (~500°C) in a furnace/heater and sent to a coker drum, where the vapor products consisting of gases and distillates are removed from the top and quenched with colder feed in the fractionator. The solid residue called coke stays in the coker drum. The feed is switched to another coker drum, once the drum in use is filled with coke. The coker drum is emptied to remove the deposited coke, and the drum is used back in the cycle. Usually, the upgrading plants have two to four coker drums. In the fluid coking process, the feed is sprayed on the fluidized hot fine coke particles in the coker vessel. Coking occurs on the surface of these particles at a temperature of ~530°C. The cracked vapors are drawn off from the top of the vessel and sent to the fractionator, after passing through a cyclone to separate the coke particles. The coke formed in this process is continuously removed from the burner vessel where it is heated to generate the hot coke, which can then be sent back to the fluidized bed to keep coking reaction continuous. The excess coke produced is removed and 25–30% of the coke is burned to generate the heat. The shorter residence time in the fluid coking process helps to maintain high temperature, higher \( \text{C}_{5+} \) liquid yield, and lower coke formation. Flexicoking is the modified fluid coking process where in place of the burner vessel, a heater and a gasifier are integrated to produce hot coke and high-value flexigas (\( \text{CO}/\text{H}_2 \)), which can be used in place of natural gas or fuel gas in refining operations. Delayed coking and fluid coking processes are mainly used for upgrading the bitumen-derived HGO. Typically, ~55 wt.% \( \text{C}_{5+} \) liquid yield and 35 wt.% coke are attained from the coking process.
The details of the thermal cracking reactions and the mechanism of coke formation were discussed by M. R. Gray in 1994.

HGO, LGO, and naphtha obtained from bitumen upgrading are blended to create the crude oil called as synthetic crude. The synthetic crude is then sent downstream to the refineries for further processing to create final products. However, before blending, HGO and LGO are hydrotreated to remove or reduce sulfur and nitrogen, and other impurities such as Ni, V, and As, which are initially present in the bitumen. The physical properties of bitumen-derived HGO and LGO are shown in Table 5.1.

### 5.2.2 Secondary Upgrading—Hydrotreating

In this process, the impurities such as sulfur, nitrogen, and metals (As, V) were removed or reduced to make the gas oil suitable for further processing in existing refineries. The major process for secondary upgrading is hydrotreating. Hydrotreating is a catalytic process in the presence of hydrogen where typically the catalyst is loaded in a fixed-bed reactor operating at high temperatures (340°C–400°C) and moderate pressures (8–10 MPa). The feed gas oil containing impurities is allowed to react with hydrogen on the catalyst surface, and the multiple reactions that take place in the reactor include hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation, hydrodemetallization, and hydrodearomatization (HDA). The conventional catalyst used for the hydrotreating reaction is molybdenum (Mo) or tungsten (W) supported on γ-alumina. The most common promoters used are nickel (Ni) or cobalt (Co) (Badoga et al. 2012). This catalyst works satisfactorily for

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>HGO</th>
<th>LGO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur (wt.%)</td>
<td>4.0</td>
<td>2.3</td>
</tr>
<tr>
<td>Nitrogen (wt.%)</td>
<td>0.37</td>
<td>0.14</td>
</tr>
<tr>
<td>Density (g/mL)</td>
<td>0.97</td>
<td>0.9</td>
</tr>
<tr>
<td>Aromatic content (%)</td>
<td>44.0</td>
<td>35</td>
</tr>
<tr>
<td>Boiling point distribution</td>
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<td></td>
</tr>
<tr>
<td>IBP (°C)</td>
<td>281</td>
<td>175</td>
</tr>
<tr>
<td>FBP (°C)</td>
<td>655</td>
<td>481</td>
</tr>
<tr>
<td>Boiling range (°C)</td>
<td>wt.%</td>
<td>wt.%</td>
</tr>
<tr>
<td>IBP–300</td>
<td>3.0</td>
<td>46.4</td>
</tr>
<tr>
<td>301–350</td>
<td>5.2</td>
<td>25.5</td>
</tr>
<tr>
<td>351–400</td>
<td>15.6</td>
<td>17.2</td>
</tr>
<tr>
<td>401–450</td>
<td>28.0</td>
<td>7.2</td>
</tr>
<tr>
<td>451–500</td>
<td>26.0</td>
<td>3.7</td>
</tr>
<tr>
<td>501–600</td>
<td>20.2</td>
<td>—</td>
</tr>
<tr>
<td>600–FBP</td>
<td>2.0</td>
<td>—</td>
</tr>
</tbody>
</table>

Sources: Narayanasarma, Prabhu, Mesoporous Carbon Supported NiMo Catalyst for the Hydrotreating of Coker Gas Oil, University of Saskatchewan, 2011; Badoga, Sandeep, Synthesis and Characterization of NiMo Supported Mesoporous Materials with EDTA and Phosphorus for Hydrotreating of Heavy Gas Oil, University of Saskatchewan, 2015. IBP, initial boiling point; FBP, final boiling point.
sweet crudes (sulfur < 0.5 wt.%). However, Table 5.1 shows that the bitumen-derived HGO contains 40,000 ppm sulfur, and as per current U.S. Environmental Protection Agency regulations, the sulfur content in diesel fuel should not exceed 15 ppm. Therefore, a highly active hydrotreating process is required to reduce the sulfur and nitrogen level of bitumen-derived gas oil to the level of conventional sweet crudes. The hydrotreating process activity can be improved by adjusting the three main parameters as shown in Figure 5.4: (1) feed pretreatment, (2) process parameter optimization, and (3) change in the catalyst. The treated oil is then further processed along with the conventional crude in existing refineries to get the final products such as diesel and gasoline. The systematic process for removal of sulfur and nitrogen from oil sands-derived gas oil is shown in Figure 5.5.

Feed pretreatment includes the removal of those impurities from oil which decreases the hydrotreating activity. For example, nitrogen, the nitrogen-containing compounds present in gas oil, severely inhibits the catalytically active sites and decreases the HDS rate. Also, as mentioned in Table 5.1, the bitumen-derived gas oil has higher nitrogen content so more inhibition is expected. Therefore, removal of nitrogen from gas oil before sending the oil for hydrotreating can increase the hydrotreating activity. Laredo et al. (2013) have
discussed in their review paper about the various types of solid adsorbent materials such as silica gel, activated carbon, ion-exchange resin, molecular sieves, and metal organic frameworks for nitrogen removal. Misra et al. (2015) have synthesized a specialty polymer for selective removal of nitrogen compounds from gas oil to adsorb and remove the nitrogen from gas oil before sending for hydrotreating. However, high cost is involved in setting up a separate unit for feed pretreatment. The second criterion is to optimize the process parameters. Usually, high temperature and pressure will result in more activity, but it severely affects the catalyst life. It also adds to higher operating costs. Moreover, increasing the temperature (above 400°C) leads to cracking, which puts limits on tuning the process parameters. The third criterion to increase the hydrotreating activity is to modify/change the catalyst. This is the most acceptable solution because after catalyst life span it needs to be changed and changing the catalyst does not involve any costs related to fixed infrastructure. Therefore, worldwide, the research is being conducted to change/modify the catalyst so as to increase the hydrotreating activity under typical industrial conditions. The improved hydrotreating process will help in producing high-quality transportation fuel from oil sands.

The hydrotreating catalyst has four main components: support material, active metals, promoter, and additives. Conventionally, γ-Al₂O₃ is used as the support. The support material not only helps in dispersion of active metals but also participates in the modification of the electronic properties, the morphology of the active phase, and the bifunctional reaction with their acid sites, which could drastically affect the catalytic activity (Badoga 2015). The Bronsted acidity in the support helps in the isomerization of alkyl groups of alkyl dibenzothiophene (DBT), which favors the removal of sulfur from these otherwise difficult-to-hydrodesulfurize molecules. The basicity of support material prevents the coke formation. The active metals such as Mo or W were sulfided to MoS₂ or WS₂ before they participate in the hydrotreating reaction, and addition of promoters such as Ni or Co enhances the hydrotreating activity. Topsoe et al. (Topsoe 2007) suggested that the active site in the NiMo/CoMo catalysts is Ni (Co)–Mo–S phase. The building blocks of the Ni–Mo–S structure are small MoS₂ nano-crystals with Ni (or Co) promoter atoms located at the edges of the MoS₂ layers in the same plane of Mo atoms as shown in Figure 5.6. It was also concluded from their studies that the relative amount of Ni atoms present as Ni–Mo–S phase was found to correlate linearly with the HDS activity.

Further studies on NiMoS active sites have revealed two types of Ni–Mo–S structures: type I and type II. Type I NiMoS sites are single layered and may be partially sulfided. These types of structures were formed when the active metal and support interaction is strong.
The strong interaction retards the reducibility/sulfidation of active metals and also results in fine dispersion of active metals. Type II NiMoS sites are two or more layered and fully sulfided (see Figure 5.7). These sites were formed when moderate-to-weak active metal and support interactions were expected. Type I and type II sites not only are different because of their structure but also favor different reactions. Type I sites tend to undergo hydrogenolysis reaction, whereas type II sites favor hydrogenation reaction (Besenbacher et al. 2008). The difference between the two reactions is shown in Figure 5.7 explaining the HDS reaction mechanism for 4,6-dimethyl dibenzothiophene (4,6-DMDBT). The hydrogenolysis route involves the direct scission of C–S bond, and it is also called direct desulfurization. However, with alkyl-substituted bulky molecules such as 4,6-DMDBT, the accessibility of sulfur to the active sites is sterically hindered. Therefore, these molecules first undergo hydrogenation to saturate the bonds and weaken the C–S bond. It is then followed by C–S bond scission to remove sulfur (Jian and Prins 1998). This reaction route is called the hydrogenation route as shown in Figure 5.7 (Egorova and Prins 2004). The understanding of HDS, HDN, and HDA reaction mechanisms is important to design a catalyst to enhance the hydrotreating activity for obtaining a high-quality liquid fuel.

The catalytic activity can be increased by (1) changing the support material, (2) adding the chelating agents such as ethylenediaminetetraacetic acid (EDTA), and (3) using promoters such as phosphorus and boron. γ-Alumina has been widely used as the support for hydrotreating reaction; however, it shows a strong metal–support interaction resulting in the formation of tetrahedral MoO$_2$ species, which are difficult to sulfide. Also, this support has a limitation of the surface area and does not have uniform pore size distribution. However, neutral supports such as SBA-15 has weak metal–support interactions resulting in poor dispersion but easier sulfidation/reduction of active metals. Therefore, the extent of metal–support interaction is very important in determining the extent of metal sulfidation/reduction during catalyst activation. For instance, molybdenum oxide on γ-alumina support starts to sulfide at 150°C; however, niobium oxide on γ-alumina is hard to sulfide at even 350°C (Allali et al. 1995). Consequently, the need for better supports that can

*FIGURE 5.7*

Hydrogenation reaction mechanism. (From Badoga, Sandeep, Synthesis and Characterization of NiMo Supported Mesoporous Materials with EDTA and Phosphorus for Hydrotreating of Heavy Gas Oil. University of Saskatchewan, 2015.)
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provide optimum metal–support interactions, high surface area, optimum pore diameter (7–15 nm), and desired acidic properties results in synthesis and testing of a large number of new materials. These include TiO$_2$, ZrO$_2$, silica–alumina, mixed oxides, carbon, SiO$_2$, zeolites, and mesoporous materials (Duchet et al. 1991; Grzechowiak et al. 2001; Carati et al. 2003). Metal oxide supports such as TiO$_2$ and ZrO$_2$ have a low surface area that limits their use; however, the activity is 3–4 times more than that shown by alumina-based catalyst (Caero et al. 2003). To utilize the properties of metal oxides and to overcome the problem of small surface area, mixed oxides including TiO$_2$–Al$_2$O$_3$ (Breyssse et al. 2003), ZrO$_2$–Al$_2$O$_3$, TiO$_2$–SiO$_2$ (Carati et al. 2003), and TiO$_2$–ZrO$_2$ are synthesized and tested by various research groups. The mixed oxides have a higher surface area and exhibit acid–base properties that are favorable for promoting desulfurization of alkyl DBTs.

Rana et al. (2003) have investigated the effects of Ni(Co)Mo catalysts supported on TiO$_2$–SiO$_2$ and ZrO$_2$–SiO$_2$ mixed oxides for hydrotreating of model compounds. They explained the role of titania and zirconia on metal dispersion and activity. In another work, Leyva et al. (2008) have synthesized and tested the NiMo/SiO$_2$–Al$_2$O$_3$ catalyst for hydrotreating of heavy oil and found it promising. Maity et al. (2006) have performed a significant work on the catalyst development for hydrotreating of Maya heavy crude. They have tested alumina–titania and titania–zirconia mixed oxides, and high surface TiO$_2$ as supports for hydrotreating catalysts. Ramirez et al. (2004) have developed the hydrotreating catalyst. They have also tested various support materials, including alumina, titania, silica–alumina for the Ni(Co)Mo(W) catalyst. In their work, they have described the electronic role played by titania in alumina framework and how it impacts the HDS activity of the supported Mo, CoMo, NiMo, and NiW catalysts. Dominguez-Crespo et al. (2008) have synthesized the NiMo catalyst using different alumina precursors and used spray and incipient impregnation methods. They have also studied the effects of pH on the catalytic activity. The results for the hydrotreating of Mexican HGO revealed an increase in HDS and HDN activities when the crystal size of the support was varied from 3 to 20 nm. They have also showed that the catalyst prepared in a basic medium performed better. Ji et al. (2004) have studied the effects of Co and Ni promotion on the hydrogenation of tetralin and the HDS of thiophene using various supported MoS$_2$ and WS$_2$ catalysts. They utilized ZrO$_2$, alumina-stabilized TiO$_2$, and pure alumina as support materials. The Ni promoted, ZrO$_2$ supported showed the highest activity. Therefore, it is evident from the literature that different supports have different metal–support interactions and hence different hydrotreating activities. Also, the catalyst performance is dependent on the type of feed gas oil.

In our work, we have synthesized various support materials, including SBA-15, M-SBA-15 (M = Ti, Al, Zr), mesoporous ZrO$_2$ and Al$_2$O$_3$, and mesoporous mixed metal oxides TiO$_2$–Al$_2$O$_3$, ZrO$_2$–Al$_2$O$_3$, and SnO$_2$–Al$_2$O$_3$ (Badoga et al. 2012; Badoga, Dalai, et al. 2014; Badoga, Sharma, et al. 2014a, 2014b; Badoga et al. 2015). The synthesis procedure of each material is mentioned in our previous work. The textural properties of each support are mentioned in Table 5.2. All the above-mentioned materials have been utilized to synthesize the NiMo-supported catalysts, and the catalysts have been tested for hydrotreating of HGO.

The hydrotreating reactions have been carried out in a laboratory-scale continuous fixed-bed reactor setup (see Figure 5.8). The setup consists of a feed tank for gas oil and a pump to transfer gas oil from the feed tank to the reactor. The hydrogen for the reaction is supplied from the tank via a mass flow controller. Post reactor there is an ammonia scrubber and then a two-phase (gas–liquid) separator. The liquid collected in the separator is removed and stripped with nitrogen before taken for analysis in Antek Nitrogen/Sulfur analyzer to measure the total nitrogen and sulfur content. The catalytic activity is
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The aromatic content of gas oil is measured using carbon-13 nuclear magnetic resonance. The activity of each catalyst for hydrotreating of HGO is reported in Table 5.3. It can be observed from the table that addition of heteroatoms such as Ti, Al, and Zr in otherwise neutral support SBA-15 has resulted in an increase in activity. This could be attributed to an increase in metal–support interactions as evident from an increase in metal dispersion (see Table 5.3). Considering the role played by heteroatoms in SBA-15 matrix, the mesoporous metal oxide support materials such as ZrO$_2$ and Al$_2$O$_3$ has been synthesized. The N$_2$ adsorption–desorption isotherm for ZrO$_2$ material has been found to be type IV with H1 hysteresis.

reported in terms of HDN, HDS, and HDA. The aromatic content of gas oil is measured using carbon-13 nuclear magnetic resonance.

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**TABLE 5.2**

<table>
<thead>
<tr>
<th>Material</th>
<th>BET Surface Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Average Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>550</td>
<td>1.10</td>
<td>6.8</td>
</tr>
<tr>
<td>TiSBA-15</td>
<td>560</td>
<td>1.20</td>
<td>7.0</td>
</tr>
<tr>
<td>ZrSBA-15</td>
<td>507</td>
<td>1.00</td>
<td>7.5</td>
</tr>
<tr>
<td>AlSBA-15</td>
<td>410</td>
<td>0.90</td>
<td>8.1</td>
</tr>
<tr>
<td>Meso ZrO$_2$</td>
<td>120</td>
<td>0.38</td>
<td>13.0</td>
</tr>
<tr>
<td>Meso Al$_2$O$_3$</td>
<td>470</td>
<td>1.00</td>
<td>6.5</td>
</tr>
<tr>
<td>Meso TiO$_2$–Al$_2$O$_3$</td>
<td>480</td>
<td>0.86</td>
<td>5.2</td>
</tr>
<tr>
<td>Meso ZrO$_2$–Al$_2$O$_3$</td>
<td>420</td>
<td>0.76</td>
<td>4.2</td>
</tr>
<tr>
<td>Meso SnO$_2$–Al$_2$O$_3$</td>
<td>450</td>
<td>0.60</td>
<td>4.1</td>
</tr>
<tr>
<td>γ-Al$_2$O$_3$</td>
<td>278</td>
<td>0.80</td>
<td>8.0</td>
</tr>
</tbody>
</table>


**FIGURE 5.8**

Hydrotreating reaction setup: Continuous fixed-bed reactor. (From Badoga, Sandeep, Synthesis and Characterization of NiMo Supported Mesoporous Materials with EDTA and Phosphorus for Hydrotreating of Heavy Gas Oil. University of Sakatchewan, 2015.)
loop, which confirmed the mesoporous structure. Also, powder wide-angle X-ray diffraction (XRD) (see Figure 5.9) has confirmed the presence of the tetragonal phase of ZrO$_2$, which is mostly the catalytically active phase (Badoga, Sharma, et al. 2014b). The surface area of zirconia has been still less than that of $\gamma$-alumina, which limits the dispersion and activity. A variety of mesoporous aluminas with different textual properties have been synthesized using a triblock copolymer as a structure direction agent. These materials have been utilized as a support for NiMo hydrotreating catalyst. The textural properties of the best material obtained are mentioned in Tables 5.2 and 5.3. The synthesis procedure plays a critical role in determining the final structure of the material, which is related to the activity. During the synthesis of mesoporous alumina, the HNO$_3$/H$_2$O ratio has been varied from 0 to 2, and it was observed that by increasing the water content in the synthesis mixture, the structure changes from an ordered hexagonal to a wormlike/spongelike to a fibular and then to a corrugated platelet/rodlike structure (see Figure 5.10) (Badoga et al. 2015).

Another class of materials tested were mesoporous mixed metal oxides. Three different types of metal oxides—TiO$_2$, ZrO$_2$, and SnO$_2$—were selected based on their increasing Lewis acidic strength, and were mixed with alumina using the direct synthesis method to get materials such as TiO$_2$–Al$_2$O$_3$, ZrO$_2$–Al$_2$O$_3$, and SnO$_2$–Al$_2$O$_3$ (Badoga, Sharma, et al. 2014a). The temperature-programmed desorption (TPD) of ammonia was performed to determine the acidic strength of catalysts supported on these materials, and the results are shown in Table 5.4. The acidic strength follows the following order: TiO$_2$–Al$_2$O$_3$$<$ZrO$_2$–Al$_2$O$_3$$<$SnO$_2$–Al$_2$O$_3$. It can be seen from Table 5.3 that the activity also follows the same order. This indicates that the activity decreases with increasing the acidic strength. This could be attributed to the inhibition of the active site by nitrogen-containing compounds present in HGO. To confirm this, acridine Fourier transform infrared spectroscopy (FTIR) was performed, and the results are shown in Figure 5.11. Acridine represents the basic nitrogen molecule. It was adsorbed on all three mixed metal oxide-supported catalysts,

### Table 5.3

Textural Properties and Hydrotreating Activity of Supported NiMo Hydrotreating Catalysts with HGO at $395^\circ$C (Catalyst = 5 cm$^3$, Pressure = 8.8 MPa, Liquid Hourly Space Velocity = 1 Hour$^{-1}$, and H$_2$/Oil Ratio = 600 [v/v])

<table>
<thead>
<tr>
<th>Material</th>
<th>BET Surface Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Average Pore Diameter (nm)</th>
<th>Metal Dispersion (%)</th>
<th>HDS (wt.%)</th>
<th>HDN (wt.%)</th>
<th>HDA (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/SBA-15</td>
<td>441</td>
<td>0.85</td>
<td>6.6</td>
<td>6.5</td>
<td>68</td>
<td>25</td>
<td>22</td>
</tr>
<tr>
<td>NiMo/TiSBA-15</td>
<td>360</td>
<td>0.88</td>
<td>7.3</td>
<td>8.8</td>
<td>82</td>
<td>42</td>
<td>27</td>
</tr>
<tr>
<td>NiMo/ZrSBA-15</td>
<td>350</td>
<td>0.72</td>
<td>7.0</td>
<td>8.8</td>
<td>73</td>
<td>36</td>
<td>30</td>
</tr>
<tr>
<td>NiMo/AlSBA-15</td>
<td>320</td>
<td>0.70</td>
<td>7.2</td>
<td>8.3</td>
<td>75</td>
<td>38</td>
<td>26</td>
</tr>
<tr>
<td>NiMo/Meso ZrO$_2$</td>
<td>90</td>
<td>0.26</td>
<td>12</td>
<td>11.0</td>
<td>89</td>
<td>47</td>
<td>25</td>
</tr>
<tr>
<td>NiMo/Meso Al$_2$O$_3$</td>
<td>345</td>
<td>0.7</td>
<td>6.1</td>
<td>19.0</td>
<td>96</td>
<td>63</td>
<td>42</td>
</tr>
<tr>
<td>NiMo/Meso TiO$_2$–Al$_2$O$_3$</td>
<td>424</td>
<td>0.41</td>
<td>4.1</td>
<td>15.0</td>
<td>96</td>
<td>62</td>
<td>63</td>
</tr>
<tr>
<td>NiMo/Meso ZrO$_2$–Al$_2$O$_3$</td>
<td>398</td>
<td>0.42</td>
<td>4.2</td>
<td>10.0</td>
<td>92</td>
<td>58</td>
<td>43</td>
</tr>
<tr>
<td>NiMo/Meso SnO$_2$–Al$_2$O$_3$</td>
<td>225</td>
<td>0.29</td>
<td>4.5</td>
<td>6.5</td>
<td>75</td>
<td>40</td>
<td>38</td>
</tr>
<tr>
<td>NiMo/γ-Al$_2$O$_3$</td>
<td>240</td>
<td>0.60</td>
<td>7.2</td>
<td>12.0</td>
<td>90</td>
<td>52</td>
<td>45</td>
</tr>
</tbody>
</table>

FIGURE 5.9
Powder wide-angle XRD pattern for (a) NiMo/Meso-Zr and (b) NiMo/Meso-Zr (EDTA). m and t represent monoclinic and tetragonal phases of zirconia, respectively. (Reprinted from Fuel, 128, Badoga, Sandeep, Rajesh V. Sharma, Ajay K. Dalai, and John Adjaye, Hydrotreating of heavy gas oil on mesoporous zirconia supported NiMo catalyst with EDTA, 30–38, Copyright 2014b, with permission from Elsevier.)

FIGURE 5.10
HRTEM micrographs for (a) Meso-Al-2, (b) Meso-Al-1.25, (c) Meso-Al-0.6, (d) Meso-Al-0.4, (e) Meso-Al-0.2, and (f) Meso-Al-0. The number at the end of each material name represents the HNO$_3$/H$_2$O ratio. (Reprinted from Appl. Catal., A: Gen., Badoga, Sandeep, Rajesh V. Sharma, Ajay K. Dalai, and John Adjaye, 489, Synthesis and characterization of mesoporous aluminas with different pore sizes: application in NiMo supported catalyst for hydrotreating of heavy gas oil, 86–97, Copyright 2015, with permission from Elsevier.)
TABLE 5.4
NH₃-TPD Results of Mesoporous Mixed Metal Oxide Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Amount of NH₃ Desorbed (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at 140°C</td>
</tr>
<tr>
<td>NiMo/Al₂O₃</td>
<td>45</td>
</tr>
<tr>
<td>NiMo/Al–Ti</td>
<td>39</td>
</tr>
<tr>
<td>NiMo/Al–Zr</td>
<td>48</td>
</tr>
<tr>
<td>NiMo/Al–Sn</td>
<td>17</td>
</tr>
</tbody>
</table>


FIGURE 5.11
and the FTIR spectra were obtained. Then all the catalysts were heated up to 350°C to
desorb the adsorbed acridine, and then again the FTIR spectra were obtained. It was
observed that the ZrO$_2$–Al$_2$O$_3$- and SnO$_2$–Al$_2$O$_3$-supported catalysts still show the peaks
related to acridine. This confirms that the nitrogen-containing compounds present in gas
oil are inhibiting the active acidic sites resulting in a decrease in activity. Therefore, for
nitrogen-rich feeds such as bitumen-derived HGO, very high acidic strength will create a
negative impact on activity. However, a slight increase in the acidic strength as shown by
TiO$_2$–Al$_2$O$_3$-supported catalyst in comparison with alumina-supported catalyst is helpful.

Further increase in the catalytic activity was achieved by using chelating ligands. As
discussed previously that NiMoS is the active site with nickel atoms decorated in the cor-
ner and edges of the MoS$_2$ slab (see Figure 5.6). During sulfidation process, nickel starts to
sulfide at 50°C and sulfidation completes at 150°C. However, molybdenum starts to sul-
fide at 150°C (Badoga et al. 2014). Therefore, early sulfidation of nickel prevents the move-
ment of nickel atoms to the corner and edges of molybdenum sulfide slabs. Consequently,
a chelating ligand is required which can delay the nickel sulfidation to the temperatures
where molybdenum starts to sulfide. Chelating ligands are those molecules that have two
or more donor atoms (dentates), which are available to bind a metal cation, for exam-
ple, EDTA. Various other chelating ligands such as citric acid, glycol, nitroacetic acid,
1,2-cyclohexanediamine-tetraacetic acid (CyDTA), and ethylenediamine were also tested
for hydrotreating catalyst. In our previous work, we studied the mechanism of interaction
between support–EDTA and EDTA–metallic species at different reaction conditions by
using different characterization techniques such as X-ray absorption near-edge structure
(XANES), high-resolution transmission electron microscopy (HRTEM), and XRD (Badoga
et al. 2012). Ni K-edge XANES analysis was performed for a series of catalysts with and
without EDTA at Canadian Light Source, Saskatoon, Saskatchewan (see Figure 5.12). Cat 0
is NiMo/SBA-15, Cat 1 is NiMo/SBA15/1EDTA with an EDTA/Ni molar ratio of 1, and
Cat 2 is NiMo/SBA15/2EDTA with an EDTA/Ni molar ratio 2. All these catalysts were
sulfided at 150°C, 250°C, and 350°C, respectively. The Ni K-edge for nickel oxide shows
an intense peak at 8355 eV corresponding to 1s to 4p electronic transitions. It was shown
in the figure that nickel oxide is converted into nickel sulfide in Cat 0 (catalyst without
EDTA) at 150°C. However, nickel in Cat 1 and Cat 2 is still in the oxide phase. At 350°C,
nickel in all catalysts is sulfided. This confirms that EDTA helps in delaying the nickel
sulfidation temperatures to the point where molybdenum starts to sulfide, thereby result-
ing in the formation of more numbers of NiMoS active sites that increase the activity as
shown in Table 5.5.

The Mo LIII-edge XANES analysis for NiMo/M-SBA-15 (M = Ti, Al, Zr) catalysts with
and without EDTA (see Figure 5.13) has confirmed that EDTA not only helps in the forma-
tion of NiMoS sites but also increases the sulfidation and number of type II NiMoS sites.
The Mo LIII-edge shows a peak at 2525 eV corresponding to 2p to 4d electronic transition
(Badoga et al. 2014). The split in the peak is due to ligand field splitting of d-orbitals. The
energy separation between the two split peaks gives the information about the structure of
molybdenum oxide. If the peak energy separation (~2.0 eV) is smaller, the structure is tetra-
hedral; if the peak energy separation (~3.0 eV) is large, the structure of molybdenum oxide
is octahedral. The octahedral structure is more desired because complete sulfidation can
be easily achieved. Also, this type of structure favors the multilayered (type II) MoS$_2$ slab
formation. It can be seen from Figure 5.13 that the catalyst NiMo/M-SBA-15 shows a smaller
energy separation in the split peak confirming the presence of predominantly tetrahedral
structure. However, while adding EDTA, the peak-to-peak energy separation in Mo LIII-
edge increases, indicating the presence of predominantly octahedral molybdenum oxide.
This concludes that EDTA helps in complete sulfidation and formation of type II NiMoS active sites, which increase the hydrotreating activity as shown in Table 5.5. Another role played by EDTA is the increase in dispersion as shown by HRTEM analysis. The HRTEM images were taken for sulfided catalysts, and the MoS₂ slab length and stacking degree distribution analysis were performed. The average slab length and stacking degree are shown in Table 5.6. It was observed that while adding EDTA, the average slab length and stacking degree decrease, which means the dispersion increases. Therefore, EDTA plays a variety of roles to enhance the hydrotreating activity. The additives such as phosphorus and boron were used to further boost the hydrotreating activity. Phosphorus is the most commonly used additive, and sometimes it is called the second promoter. Various other

![Diagram](image.png)

**FIGURE 5.12**
XANES spectra of sulfided Ni K-edge of (a) catalysts at 150°C, (b) catalysts at 250°C, and (c) catalysts at 350°C. (Reprinted from *Appl. Catal., B: Environ.*, Badoga, Sandeep, K. Chandra Mouli, Kapil K. Soni, a.K. Dalai, and J. Adjaye, 125, Beneficial influence of EDTA on the structure and catalytic properties of sulfided NiMo/SBA-15 catalysts for hydrotreating of light gas oil, 67–84, Copyright 2012, with permission from Elsevier.)
TABLE 5.5
Hydrotreating Activities of Mesoporous Material-Supported NiMo Hydrotreating Catalysts with and without EDTA with HGO at 395°C (Catalyst = 5 cm³, Pressure = 8.8 MPa, Liquid Hourly Space Velocity = 1 hour⁻¹, and H2/Oil Ratio = 600 [v/v])

<table>
<thead>
<tr>
<th>Material</th>
<th>HDS (wt.%)</th>
<th>HDN (wt.%)</th>
<th>HDA (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/SBA-15</td>
<td>68</td>
<td>25</td>
<td>22</td>
</tr>
<tr>
<td>NiMo/SBA-15/EDTA</td>
<td>78</td>
<td>32</td>
<td>27</td>
</tr>
<tr>
<td>NiMo/TiSBA-15</td>
<td>82</td>
<td>42</td>
<td>27</td>
</tr>
<tr>
<td>NiMo/TiSBA-15/EDTA</td>
<td>95</td>
<td>54</td>
<td>32</td>
</tr>
<tr>
<td>NiMo/Meso ZrO₂</td>
<td>89</td>
<td>47</td>
<td>25</td>
</tr>
<tr>
<td>NiMo/Meso ZrO₂/EDTA</td>
<td>94</td>
<td>55</td>
<td>40</td>
</tr>
<tr>
<td>NiMo/γ-Al₂O₃</td>
<td>90</td>
<td>52</td>
<td>45</td>
</tr>
<tr>
<td>NiMo/γ-Al₂O₃/EDTA</td>
<td>94</td>
<td>58</td>
<td>50</td>
</tr>
</tbody>
</table>


FIGURE 5.13
XANES spectra of Mo LIII-edge of (a) catalysts with EDTA and (b) catalysts without EDTA. (Reprinted with permission from Badoga, Sandeep, Ajay K Dalai, John Adjaye, and Yongfeng Hu, *Ind. Eng. Chem. Res.*, 53, 2137–2156. Copyright 2014 American Chemical Society.)
types of catalysts such as trimetallic (NiMoW, NoCoMo) supported sulfided catalysts and supported nickel tungsten phosphides were also tested for hydrotreating of gas oil, which have shown promising results.

Therefore, hydrotreating is a very important process in producing the clean liquid fuels from oil sands because it improves the properties of bitumen-derived crude to match with the properties of conventional crude oil. Hydrotreating process reduces the sulfur and nitrogen level of (1) LGO to 65 and 25 ppm from 23,000 and 1400 ppm, respectively, and (2) HGO to 2330 and 1330 ppm from 40,000 and 3700 ppm, respectively. The upgrading process also helps to increase the API gravity from 8.5° of bitumen to 36.2° for LGO and 22.5° for HGO (Product Specification 2015). The hydrotreated LGO and HGO and naptha were blended to make synthetic crude with an API gravity of 34°, and containing the sulfur and nitrogen level of 1400 and 440 ppm, respectively. The synthetic crude is sent to refineries where it is processed to obtain fuel fractions such as gasoline, diesel, kerosene, jet fuels, and petrochemicals. Hence, hydroprocessing makes the oil usable by the existing refineries to produce environmentally safe liquid fuels.

### 5.3 Challenges and Opportunities in Oil Sands Industry

The extraction of liquid fuels from oil sands, however, has many challenges, including bigger environment footprint, tailing ponds, water usage, technological limitations, land reclamation, and coke production. The extraction of oil from oil sands is energy intensive and adds the bigger environmental footprint compared to the conventional oil extraction process. Therefore, it is important to innovate and develop a technology which has minimal impact on environment. The research is being carried out to find effective ways to increase the efficiency of in situ extraction by modifying the steam system or by using an alternate heating method (Impiantistica Italiana-Settembre-Ottobre 2013). The oil extraction process generates a mixture of water, salts, chemicals (such as benzene, naphthalene, phenol, and hydrocarbons), clay, sand, and slit in large quantities, and it is stored or processed in tailing ponds. The process-affected water in the tailing ponds is being reused, which decreases the amount of freshwater required for oil extraction process. However, with an increase in oil production, the size of the tailing ponds is increasing. Currently, in Alberta, Canada, the tailing ponds covered an area of nearly 77 km² (Oil Sands Tailings 2013). The increasing size of the tailing ponds is the major and most difficult environmental

#### TABLE 5.6

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average Length (nm)</th>
<th>Average Stacking (Number of Layers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/SBA-15</td>
<td>6.2</td>
<td>4.6</td>
</tr>
<tr>
<td>NiMo/SBA-15/EDTA</td>
<td>4.8</td>
<td>2.9</td>
</tr>
<tr>
<td>NiMo/TiSBA-15</td>
<td>4.8</td>
<td>3.2</td>
</tr>
<tr>
<td>NiMo/TiSBA-15/EDTA</td>
<td>3.6</td>
<td>2.0</td>
</tr>
</tbody>
</table>

challenge faced by an oil sands mining sector. The regulations are forcing to reduce the size of the tailing ponds and transform the nonused tailing ponds to the reclaimed land. Therefore, intensive research and development is being carried out in this area, which is mostly focused on separation of solids, biological, and chemical treatments.

The process of extracting liquid fuels from oil sands produces asphaltenes and coke as major by-products. The asphaltenes are used as paving materials on roads, roof shingles, and building foundation waterproofing. However, the challenges are associated with coke utilization, and its storage is a concern for upgraders (Andrews and Lattanzio 2013; Khosravi and Khadse 2013; Murthy et al. 2014). The coke produced during upgrading contains 6–7 wt.% sulfur and metals such as nickel and vanadium, which make it difficult to use by steel and aluminum industries, which require low sulfur and pure coke. However, majority of the petroleum coke is utilized as a fuel, and cement and power plants are the major consumers. Researchers are trying to find the alternate use of raw petroleum coke, which includes the gasification of petroleum coke to produce synthesis gas, which is then converted to liquid fuels via Fischer–Tropsch synthesis (Khosravi and Khadse 2013; Murthy et al. 2014), and the synthesis of activated carbon from coke (Rambabu et al. 2014).

### 5.4 Summary

Extracting liquid fuels from oil sands is an energy-intensive process compared to obtaining liquid fuels from conventional resources. The hydrocarbon content of oil sands called bitumen is extracted via two main techniques: (1) surface mining and (2) SAGD. For deep bitumen reservoirs, the SAGD process is preferred. The bitumen is very thick and highly viscous to flow, and has an API gravity of less than 10°. It also contains very high amount of sulfur (4–6 wt.%) and nitrogen (0.3–0.6 wt.%). To extract the crude oil from bitumen that can be processed in existing refineries, the bitumen is upgraded in two steps: primary upgrading and secondary upgrading. Primary upgrading includes the fractionation of bitumen mainly into naphtha, LGO, and HGO, and the removal of excess carbon in the form of coke and asphaltene. The obtained LGO and HGO still have very high sulfur and nitrogen content compared to conventional crude oil. Therefore, secondary upgrading of LGO and HGO was performed to reduce the impurities. This includes hydrotreating, which is a catalytic process. The higher hydrotreating efficiency determines the product quality and hence profitability. Therefore, intensive research is performed in catalyst modification and development, which includes modification in support materials, active metals, and use of additives. Various supports, including mesoporous materials (SBA-15, Al-SBA-15), mesoporous metal oxides (Al₂O₃, TiO₂, ZrO₂), and mixed metal oxides (TiO₂–Al₂O₃, ZrO₂–TiO₂, TiO₂–SiO₂, ZrO₂–Al₂O₃), have been extensively studied for hydrotreating of gas oils derived from oil sands. It was observed that alumina-based supports perform better in hydrotreating reactions. The addition of chelating ligands (EDTA) and additives (phosphorus and boron) have significantly improved the hydrotreating activity of bitumen-derived HGO. The difference in the hydrotreating activity of various catalysts is well explained using detailed characterization techniques such as, Brunauer-Emmett-Teller (BET), XRD, temperature programmed reduction (H₂-TPR), FTIR, RAMAN, NH₃-TPD, CO chemisorption, HRTEM, and XANES. After hydrotreating, LGO, HGO, and naphtha were mixed to form synthetic crude having less sulfur and nitrogen, and an API.
gravity of 34°. The synthetic crude is then processed in refineries to obtain final product liquid fuels such as diesel, gasoline, kerosene, and petrochemicals. The oil sands industry faces many challenges such as tailing ponds, water usage, technological limitations, land reclamation, and large amount of coke production. However, worldwide concerns for deteriorating environment and global warming bring the motivation (1) to explore non-fossil-based energies such as solar and wind, and (2) to innovate an improved technology for extracting and purifying liquid fuels derived from nonconventional resources such as shale oil and oil sands.

References


