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Escuela de Ciencias Químicas e Ingeniería

Study of aluminum – pillared clays as catalyst supports for hydrodesulfurization and catalytic activity

Trabajo de integración curricular presentado como requisito para la obtención del título de Petroquímico

Autor:

Erick Damián Criollo Amaguaña

Tutor:

PhD. Dario Alfredo Viloria

Co-Tutor:

PhD. Ernesto Bastardo - González

Urcuquí, Julio 202



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CI: 1804474995

DEDICATION

To my parents and sister for their advice, unconditional support and patience.

Erick Damian Criollo Amaguaña

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RESUMEN

Las exigentes normas regulatorias de emisiones contaminantes han obligado a la búsqueda de nuevos catalizadores de hidrotratamiento más activos y resistentes a la desactivación catalítica. Las arcillas pilareadas han sido ampliamente utilizadas en procesos de adsorción debido a su alta área superficial, tamaño de poro, fuerte superficie ácida y gran estabilidad térmica. Estas características hacen que sean un material atractivo para usos catalíticos en procesos como la hidrodesulfuración. El presente trabajo consistió en una revisión bibliográfica sobre los diferentes usos que han tenido las arcilla como soporte de catalizadores para procesos de refinería, con especial énfasis en hidrotratamiento. El trabajo resume aspectos como la problemática del azufre, síntesis de arcillas pilareadas, preparación de catalizadores soportados en arcillas pilareadas, actividad catalítica en hidrotratamiento y una visión general de las arcillas en el Ecuador. Los estudios revisados muestran que los catalizadores comerciales, sin embargo, la preparación a nivel industrial aun no es viable debido al tiempo y la cantidad de agua necesaria.

Palabras clave: Arcillas pilareadas, catalizadores para hidrodesulfuración, azufre, Ecuador

ABSTRACT

Stringent regulatory standards for pollutant emissions have forced the search for new hydrotreating catalysts that are more active and resistant to catalytic deactivation. Pillared clays are widely used in adsorption processes due to their high surface area, pore size, strong acid surface area, and high thermal stability. These characteristics make them an attractive material for catalytic uses in processes such as hydrodesulfurization. The present work consisted of a bibliographic review of the different uses of clay as catalyst support for refinery processes, emphasizing hydrotreating. The work summarizes aspects such as sulfur problems, synthesis of pillared clays, preparation of catalysts supported on pillared clays, catalytic activity in hydrotreatment, and an overview of clays in Ecuador. The reviewed studies show that catalysts supported on pillared clays show higher catalytic activity than commercial catalysts. However, the industrial level preparation is not yet feasible due to the time and amount of water required.

Keywords: Pillared clays, hydrodesulfurization catalysts, sulfur, Ecuador.

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CHAPTER I

INTRODUCTION

1.1. Problem Statement

Catalytic processes are fundamental to obtain high value products within a refinery. Processes such as catalytic cracking, reforming, and hydroprocessing use catalysts to led the main reaction towards the desired products. Hydrotreating removes undesirable impurities from the oil, especially heteroatoms such as sulfur, nitrogen, oxygen, and heavy metals. Sulfur concentrations can vary between 0.05 and 6 wt. %. The maximum sulfur content is found in the heavier fractions of the oil, mainly in the form of refractory molecules such as thiophenes, benzothiophenes, and polysubstituted dibenzothiophenes.

Sulfur and coke are the main deactivating agents of the catalysts used in the refinery, in addition of contributing to corrosion problems. Also, sulfur oxides produced after the combustion of fossil fuels generate environmental problems such as acid rain and contribute to global warming, as well as respiratory and cardiovascular problems in humans.

Worldwide, the automotive sector is considered to be the main emitter of SOx into the atmosphere. As a consequence, the first Euro standard came into force in Europe in 1992 intending to control pollutant emissions generated by vehicles powered by fossil fuel combustion. Since then, this standard has evolved into stricter and stricter standards until it has become a worldwide reference. Currently, the Euro 6 standard came into force in 2014.

In Ecuador, the current regulations governing sulfur content in gasoline and diesel are the NTE INEN 935 and NTE INEN 1489:2012 standards, respectively. These standards are homologated to the Euro 3 standard, which indicates that Ecuador is 20 years behind developed countries. As a result, Ecuador has one of the lowest quality fuels in the region. This is probably because that the country's refineries do not have the necessary conditions to meet stricter specifications.

Hydrodesulfurization is an essential process to meet the strict standards applied to fossil fuels. NiMo or CoMo catalysts supported on γ -Al₂O₃ are the most used in hydrotreatment processes, however, alternative catalysts supported on clays and pillared clays have been proposed to remove as much sulfur as possible and more resistant to

deactivation. On the other hand, in Ecuador, the information on the use of clays as catalytic agents is very scarce, since the main use is the production of cement and fine ceramics.

Therefore, it is necessary to analyze the use of pillared clays as catalyst support for hydrodesulfurization. In this way, it is intended to take advantage of the abundance of smectite-type clays in Ecuador. Following with the challenge of preparing catalysts that are more active and resistant to deactivation.

1.2. Objectives

1.2.1. General Objective

To give an overview of the research carried out on the use of pillared clays as catalyst support for refinery processes, with special emphasis on hydrotreating.

1.2.2. Specific Objectives

- To compile information about catalysts supported on pillared clays.
- To synthesize information about the deposits and the principal uses in Ecuador of smectite clays.
- To analyze if clays in Ecuador can be used as support for catalysts.

CHAPTER II

LITERATURE REVIEW

2.1. Petroleum

Petroleum is a complex mixture of hydrocarbons in a liquid state, with small amounts of nitrogen, sulfur, oxygen, heavy metals, and others, which are accumulated in subway reservoirs. Crude oil exhibits a wide variety of properties that prevent its use in its natural state; therefore, it must be transformed into value-added products that can be used in the market. After the refining process, refinery gas, LPG, naphtha, gasoline, jet fuel, fuel oil, gas oil, diesel, residual fuel oil, lubricants, asphalt and coke are obtained. From the molecular point of view, there are three types of hydrocarbons present in crude oil:

- Paraffins: these are saturated hydrocarbons, rich in hydrogen and perfectly stable; their general formula is C_nH_{2n+2}.
- Naphthenes: are saturated cyclic hydrocarbons; their general formula is C_nH_{2n}.
- Aromatics: are unsaturated cyclic hydrocarbons. They contain a benzene ring that allows them to behave as saturated; their general formula is C_nH_{2n-6} .

Besides, a fourth type is formed only in the cracking or dehydrogenation of kerosenes and naphthenes [1].

- Olefins: are unsaturated hydrocarbons, very reactive and combine easily with hydrogen, oxygen, chlorine, sulfur. The general formula is: C_nH_{2n} .

The Watson factor (K_W) estimates the character and behavior of crude oil, based on a relationship between boiling point and specific gravity. A K_W factor of less than 10 corresponds to highly aromatic compounds, a range from 10.5 for highly naphthenic crudes to 12.9 for paraffinic crudes and 15 for highly paraffinic crudes [2].

2.1.1. API Gravity

API gravity allows the relative density of various petroleum liquids to be measured; it is related to specific gravity. The API gravity specifies how light or heavy the oil is, and indirectly gives an idea about its composition, as light crudes often have low sulfur concentrations as opposed to heavy crudes. According to American Petroleum Institute (API), crude oils can be classified into [3]:

- Extra-Heavy Oil: < 10 °API
- Heavy Oil: 10 22.3 °API
- Intermediate Oil: 22-31.1 °API
- Light Oil: > 31.1 °API

From the extraction point of view, heavy and extra-heavy oils present problems in the transportation to storage tanks due to their low fluidity, in addition to the associated corrosion problems. For this reason, techniques have been developed to reduce viscosity employing steam injection or additives, facilitating not only extraction and subsequent transportation, but also the oil recovery rate. These processes require additional equipment to maintain adequate viscosity through temperature. In contrast, light crude oils have almost no such operational problems [4].

The physicochemical characteristics of oil influence the economic context. Generally, light crudes have a higher price than heavy and extra-heavy crudes. Light oil provides large amounts of light distillates together with small amounts of organic nitrogen, oxygen, sulfur and trace amounts of organometallic compounds (vanadium, nickel, lead); thus, allowing lower production costs. Mainly gasoline, diesel and heavy fuel components are obtained. On the other hand, heavy oil tends to have higher concentrations of metals and refractory molecules, low-value products, which require more effort in the refining process to obtain the desired products.

The variation in the price of oil produces uncertainty in refineries about the type of oil that should be used to obtain quality products. Purchasing quality oil at a premium or assuming high refining costs due to the low quality of the raw material.

2.1.2. World oil reserves

The growing demand for oil and the decline of light oil deposits have led to an increase in exploration and extraction of heavy oil wells in recent years. However, heavy oil presents problems not only in the reservoir but also in transportation and refining. These problems are associated with sulfur and heavy metal issues resulting in technical difficulties and high production costs due to additional processes and treatments to reach quality standards.

It is currently estimated that oil reserves in the world are between 9 and 13 trillion barrels, of which 30% corresponds to conventional resources and the remaining 70% are unconventional resources. The unconventional resources are distributed in 15% heavy oil, 25% extra-heavy oil, 30% oil sand and bitumen. It is estimated that the reserves of heavy oil and bitumen are 5.9 trillion barrels, of which 80% are found in Venezuela, Canada and USA [5] [6]. The CIA's World Factbook shows the numbers and type of crude oil reserves of countries in the world (Figure 1). Nonetheless, large oil reserves do not mean wealth, as in Venezuela and Canada, whose production costs are high because they come from oil sands.



World Oil Reserves

Figure 1. World oil reserves [7].

Venezuela has the world's single largest oil accumulation, in the Faja Petrolifera del Orinoco. The total estimated oil in place is 1.2 trillion barrels of which 310 billion barrels are recoverable resources. In the last two decades, oil production has declined to less than 1 million barrels per day. Canada, on the one hand, has large in situ bitumen and extra-heavy reserves which are 165 billion barrels; besides, estimated in situ resources in Alberta are 1845 billion barrels. It is expected to achieve an increase in production of up to 3.8 million barrels

of marketable bitumen per day by 2025. On the other hand, the USA contains several heavy crude oil reservoirs. The proved reserves in California are 2.854 million barrels while the undeveloped shallow bitumen deposits are estimated at 4.7 billion barrels. The most important deposits are Midway-Sunset, Kern River and South Belridge [8].

2.1.3. Ecuador oil reserves

The oil boom in Ecuador began in 1972, when 42 million barrels were exported, the same amount that was exported between 1928 and 1957. Up to that time, oil represented between 1% and 3% of the Gross domestic product (GDP) [9]. After the oil boom, an aggressive exploration campaign began in the Orient and the state granted concessions to private companies. Ecuador experienced a period of bonanza and became an oil-dependent country, eventually in 2008 20% of the GDP was based on oil exploitation. Today, oil accounts for 35% of Ecuador's total exports [10]. Over the next 4 decades, the country's economy has risen and fallen along with oil. In the last decade, due to continuous constitutional reforms and economic instability, exploration of new fields has ceased and reserves are estimated at 8,273 billion barrels [7]. Oil production in the last decade can be seen in Figure 2.



Figure 2. Daily production in the last decade in Ecuador [7].

National crude oil production, in the first quarter of the year 2020 reached 48.9 million barrels, 2.7% more than the first quarter of 2019. However, such increase would be affected after the rupture of both pipelines: Sistema de Oleoductos Trans Ecuatorianos (SOTE) and the Oleoducto de Crudos Pesados (OCP). These ruptures reduced production by 205,240 barrels of the 429,172 barrels per day that were being produced. After the rupture, the oil Gross Value Added (GVA) decreased 29.4% and added to the context of the pandemic the GDP decreased by 12.4% concerning 2019 [11]. This shows how susceptible Ecuador is to changes in oil production and price. Figure 3 shows the variations of GDP in the period 2017-2019. In July of the same year, production returned to 423 494 barrels per day by national companies while 105 807 barrels per day by private companies. Total barrels produced are 529 301 barrels per day [12].



Figure 3. GDP decline in the second quarter of 2020 [11]

According to Petroamazonas [13], oil reserves are estimated to reach 1 495 MMBls in proven reserves, 245 MMBls in probable reserves and 702 MMBls in possible reserves. As of December 31, 2016, cumulative production was 4 630 MMBls. As for gas reserves, 184 470 MMSCF in proved reserves, 173 994 MMSCF in probable reserves and 116 765 MMSCF in possible reserves are estimated, with approximate production amounting to 180 186 MMSCF. In addition, contingent resources amount to 1.194 MMBls, with cumulative

production of 2 MMBls. On the other hand, the estimated volume of prospective resources analyzed is 1,932 MMBls, of which 1,273 MMBls are unrisked prospective resources and 659 MMBls are risked prospective resources. The total sum of 3P reserves, contingent resources and prospective resources amount to 4 819 MMBls.

Two main types of crude oil are produced in Ecuador: Oriente and Napo. Oriente crude oil is the commercial name given to the blend of several crudes that reach an average gravity of 24° API. Although at its beginnings this crude oil reached 29° API, it has gradually been reduced. It comes mainly from fields located in the Oriente base such as Lago Agrio, Tambococha, Tiputini, Auca, Culebra-Yulebra-Anaconda, Shushufindi-Aguarico, Cuyabeno - Sansahuari, Sacha and Ishpingo [14]. On the other hand, Napo crude has 17° API, so its price in the international market is much lower than West Texas Intermediate (WTI). Figure 4 shows the reserves of some of the wells mentioned above.



PRODUCCIÓN ACUMULADA POR ACTIVO AL 31 DE DICIEMBRE DE 2016

Figure 4. Reserves of some oil wells in Ecuador [13].

2.2. Sulfur

Of all the heteroatoms compounds in oil, sulfur has the most important effect on the refinery. The most important drawbacks are deactivation by poisoning of catalysts, corrosion of refinery equipment, and emission of sulfur compounds into the atmosphere [3]. Refineries are constantly increasing efforts to reduce the sulfur content in their products as much as possible, due to stringent regulations issued by environmental authorities. Figure 5 shows the corrosion problem associated with H_2S .



Figure 5. H₂S corrosion in pipelines [15].

The sulfur content of crude oil is usually between 0.2 wt.% and 3.0 wt.% Generally, sweet crude is used commonly to name crudes with sulfur content less than 0.5% wt., and sour crude for values greater than 1.5 wt.%. Certain petroleum products need very low sulfur content to comply with established standards, for this reason, the refining costs of sour crudes tend to increase due to additional sulfur removal treatments compared to sweet crudes. Table 1 shows the sulfur index of the most representative crudes in the international market.

	Ocumentary of		Properties	
Crude Oil	Origin Crude Oil Class		Gravity (°API)	Sulfur (wt.%)
Brent West Texas Intermediate	U.K. U.S.A.	Light Sweet	40.0 39.8	0.5 0.3
Arabian Extra Lt. Export	Saudi Arabia	Light Sour	38.1	1.1
Daqing	China	Madium Madium Sour	33.0	0.1
Forcados Export	Nigeria	Medium Medium Sour	29.5	0.2
Arabian Light Export Kuwait Export Blend	Saudi Arabia Kuwait	Medium Sour	34.0 30.9	1.9 2.5
Marlim Export Cano Limon	Brazil Colombia	Heavy Sweet	20.1 25.2	0.7 0.9
Oriente Export Maya Heavy Export	Ecuador Mexico	Heavy Sour	25.0 21.3	1.4 3.4

Table 1. Gravity °API and sulfur levels present in some important types of crude oil [16].

The refining process starts with the desalting of the crude oil, then the stream enters the atmospheric distillation where different fractions of crude oil are obtained. The fractions obtained are gas, naphtha, kerosene, atmospheric gas oil, vacuum gas oil. These fractions are characterized by their boiling point and generally contain traces of heteroatoms such as sulfur and nitrogen (Table 2) [17]. These streams are sent to other towers and units to undergo new processes, at the end of which oil derivatives will be obtained.

Table 2. Properties of crude fractions [17].

	Naphtha	Kerosene	Gas oil	Atmospheric residue	Vacuum gas oil	Vacuum residue
Boiling point (°C)	40-180	180-230	230-360	343+	343-500	500+
% of S	0.01-0.05	0.1-0.3	0.5-1.5	2.5-5	1.5-3	3-6
% de N	0.001	0.01	0.01-0.05	0.2-0.5	0.05-0.3	0.3-0.6

2.2.1. Sulfur Compounds

Sulfur in oil occurs in various forms, such as hydrogen sulfide, hydrogen sulfide, mercaptans, sulfides, disulfides, while in the heavier fractions there are refractory compounds such as thiophenes, polysubstituted benzothiophenes and dibenzothiophenes, which due to their complex structure are very stable and not very reactive (Figure 6).



Figure 6. Most common sulfur compounds in crude oil.

Several methods are currently available to characterize and quantify sulfur content in fuels. Standardized assays such as ASTM D129, ASTM D1552, ASTM D4249 require high-temperature treatment of the samples, moreover, methods such as wavelength dispersive X-ray fluorescence spectrometry (WDXRF) and energy dispersive X-ray fluorescence spectrometry (EDXRF) are used due to the absence of such treatment [18].

Over the years, sulfur removal has developed due to the stringent environmental regulations that have been implemented. The literature shows several related processes, such as hydrodesulfurization (HDS), oxidative desulfurization (ODS), adsorption desulfurization, biodesulfurization. The most widely used removal method in refineries is hydrodesulfurization due to the performance obtained compared to other options, although it should be noted that it has high operating costs.

2.2.2. Regulation

The first regulations on fossil fuels were not only introduced to reduce pollution but also because they did not allow the use of new technologies. Proof of this is the restriction of lead in the '70s that prevented the use of catalytic equipment, as well as the use of methyl tert-butyl ether (MTBE) as oxygenating in gasoline due to its toxicity to humans. Currently, efforts are being made to reduce CO and NOx emissions, but sulfur inhibits the use of technologies to achieve it.

Sulfur oxides (SOx) affect the performance of catalytic converters, producing corrosion problems in pipes, engines and equipment. They are also harmful to the environment, as they are the main cause of acid rain and cause respiratory problems in humans. For these reasons, stringent fuel standards have been implemented and scientific efforts have focused on more effective catalysts to achieve the desired quality.

European Union implemented the Euro 1 standard in 1992. Euro standards are a set of requirements that regulate the acceptable limits for internal combustion gas emissions. Since then, these standards have been renewed every 4 years with new requirements that vehicles must meet. In addition to prohibitions and restrictions on the circulation of vehicles. These standards have been a worldwide reference and currently have the Euro 6 standard.

By comparison, the United States uses ASTM standards, such as D 4814, which is the standard for gasoline, D 975, which regulates diesel fuels, and D1655, which covers jet fuels. Even D 6751 has been proposed for biodiesel fuel blends.

Since the information is scattered, the European Automobile Manufacturers Association [19] synthesizes the main standards in the world by grouping them into categories. The categories are listed below:

- Category 2: Markets with requirements for emission control, such as US Tier 1, Euro
 2, Euro 3 or equivalent emission standards, or other market demands.
- Category 3: Markets with more stringent requirements for emission control, such as US LEV, California LEV or ULEV, Euro 4 (except lean burn gasoline engines), JP 2005 or equivalent emission standards, or other market demands.
- Category 4: Markets with advanced requirements for emission control, such as US Tier 2, US Tier 3, California LEV II, Euro 4, Euro 5, Euro 6/6b, JP 2009 or equivalent emission standards, or other market demands. Category 4 fuels enable sophisticated NOx and particulate matter after-treatment technologies.

- Category 5: Markets with highly advanced requirements for emission control (including GHG) and fuel efficiencies, such as US Tier 3 Bin 5, US light-duty vehicle fuel economy, California LEV III and as amended, Euro 6c, Euro 6dTEMP, Euro 6d, current EU CO₂ target, China 6a, China 6b or equivalent emission control and fuel efficiency standards.
- Category 6: Markets with potential emission control and fuel efficiency targets more stringent than those in Category 5, such as future or anticipated US light-duty vehicle GHG and fuel economy standards and future EU targets for CO₂.

Examples of trace metals include, but are not limited to, Cu, Fe, Mn, Na, P, Pb, Si and Zn. No trace metal should exceed 1 ppm.

Gasoline and diesel have quality indicators, such as octane number and cetane number respectively. The octane number is a scale that measures the anti-knock capability of fuel when compressed inside the cylinder of an engine. The cetane number is an indicator of the rate of combustion of diesel fuel, and the compression required for ignition. This number is related to the time that elapses between the injection of the fuel and the start of its combustion, called the ignition interval. On the other hand, standards have imposed restrictions on the maximum number of oxygens, olefins, aromatics, sulfur and trace metals. Table 3 and Table 4 show the quality requirements for each of the above-mentioned categories of the both gasoline and diesel fuels.

Gasoline						
	Category 2	Category 3	Category 4	Category 5	Category 6	
Sulfur, ppm	150	30	10	10	10	
Oxygen, %m/m	2.7	2.7	2.7	3.7	3.7	
Olefins, %v/v	18.0	10.0	10.0	10	10.0	
Aromatics, %v/v	40.0	35.0	35.0	35.0	35.0	
Benzene, %v/v	2.5	1.0	1.0	1.0	1.0	
RON	91, 95, 98	91, 95, 98	91, 95, 98	95, 98	98, 102	

Diesel						
	Category 2	Category 3	Category 4	Category 5		
Cetane Number	51	53	55	55		
Sulfur, ppm	300	50	10	10		
Total aromatics %m/m	25	20	15	15		
Flash point, °C	55	55	55	55		
FAME, %v/v	5	5	5	Non-detectable		
Distillation T90 °C	340	320	320	320		
Distillation T95 °C	355	340	340	340		

Table 4. Diesel emission control requirements [19].

Similarly, Ecuador has implemented fuel quality standards to be marketed in the country. NTE INEN 935 [20] establishes requirements for 87 octane, 92 octane and 93 octane gasoline. NTE INEN 1489:2012 [21] in addition to the quality requirements, indicates the use of each type.

- Diesel No. 1: fuel used in industrial or domestic external combustion appliances.
- Diesel No.2: fuel used in the industrial, fishing and electrical sectors, except for the automotive sector.
- Diesel Premium: fuel used in automotive vehicles.

While the price of fuels in Ecuador is approaching international prices, their quality is questionable. Ecuador has some of the worst fuels in the region, which damages engines and affects the environment and people's health. According to INEN standards, gasoline quality is EURO 2 type, which indicates a 20-year delay, while diesel is EURO 1 type. Table 5 and Table 6 show the quality of fuels sold in the country.

Gasoline								
	87 Octane 92 Octane 93 Octane							
Sulfur, ppm	65	65	30					
Oxygen, %m/m	2.7	2.7	2.7					
Olefins, %v/v	18.0	25	25					
Aromatics, %v/v	30.0	35.0	35.0					
Benzene, %v/v	1	2.0	1.3					
RON	87	92	93					

Table 5. Gasoline Specifications according to NTE INEN 935

Table 6. Diesel Fuel Specifications according to NTE INEN 1489:2012

Diesel						
	Diesel No. 1	Diesel No. 2	Diesel Premium			
Cetane Number	40	45	45			
Sulfur, % w/w	0.3	0.7	0.05			
Flash point, °C	40	51	51			
kinematic viscosity, cST	3	6	6			
Distillation T90 °C	288	360	360			

2.3. Hydrodesulfurization

Hydrodesulfurization is a crude oil purification process that mainly removes sulfur, but at the same time denitrification, deoxygenation and cracking reactions are carried out. The main objective of this process is to protect the catalysts used in the refinery's catalytic processes, and also to remove sulfur compounds to comply with regulations. However, to increase sulfur removal greater operational efforts are required, which increase costs and risks in the facilities.

Despite advances in the catalytic industry, it is still impossible to obtain sulfur-free refinery products. This is because a percentage of sulfur belongs to refractory molecules of high boiling points and highly substituted, causing these molecules to have high steric hindrance and to be very unreactive. A wide range of refractory molecules, mainly alkylsubstituted dibenzothiophenes (DBT), such as 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) are found in the heavier fractions of crude oil, corresponding to the majority of residual sulfur in refined crude oil [22] [23].

Hydrodesulfurization consists of the reaction of hydrocarbons with hydrogen in the presence of an appropriate catalyst bed. The feed typically consists of fractions from primary distillation, prior to any catalytic process. The products of the process are desulfurized gasoline, desulfurized light and heavy naphtha, or desulfurized fuel oils or desulfurized catalytic fuel oils; on the other hand, sulfur is removed in the form of hydrogen sulfide [24]. Generally, this process is carried out at temperatures ranging from 330°C to 400°C and pressures in the range of 5 to 10 MPa [25]. Figure 7 illustrates a typical hydrotreating unit.

The most important process variables in HDS are temperature, hydrogen partial pressure and space velocity. Increasing temperature facilitates the HDS reaction, avoiding excessive temperatures due to increased coke formation and consequent catalytic deactivation. Hydrogen partial pressure increases at HDS reaction rate, and reduces poisoning by coke deposition. High pressures promote the HYD mechanism, avoid reaction temperature increase and reduce coke formation on the catalyst. Decreasing the space velocity enhances the HDS activity because it increases the contact time between the phases and the catalyst [26].



Figure 7. Catalytic hydrodesulfurizer system [25]

2.4. HDS Catalyst

2.4.1. Catalyst Structure

A catalyst is a substance that increases the reaction rate, without being consumed in the process. The solid catalyst usually consists of:

- The active phase reduces the activation energy of a chemical reaction. They can be metals, metal oxides, metal sulfides or metal carbides.
- The promoter modifies support or active phase properties. The properties may be activity, selectivity or resistance to deactivation.
- The support facilitates dispersion and stability of the active phase. It generally has a high surface area, adequate pore size distribution and suited thermal stability.

The catalysts used in refineries allow increasing the speed and selectivity of the reactions carried out in the HDT stage. The most commonly used catalysts for HDT are molybdenum sulfides, promoted with Ni or Co. The main difference between both Ni-Mo and Co-Mo catalysts is their hydrogenation activity. Co-Mo catalysts have high activity for HDS at mild conditions with minimal hydrogen consumption, but are sensitive to refractory compounds such as DBT. In contrast, Ni-Mo catalysts allow higher hydrogenation of the aromatic ring obtaining better HDS activity for refractory compounds via HYD. However, they have high hydrogen consumption.

2.4.2. Catalyst Preparation

Bimetallic catalysts are often synthesized by the sequential incipient impregnation method. This method consists of impregnating the support with Mo through a precursor. After drying and calcining, Co or Ni impregnation is carried out, and the drying and calcining process are repeated. The catalysts impregnated first with Co or Ni show lower activity than catalysts with primary Mo impregnation. This indicates that the order of impregnation influences the catalyst.

Another method of catalyst synthesis is co-impregnation, which consists of simultaneous impregnation of precursors in an aqueous state, followed by drying and calcination. It has been shown that the activity of the catalyst depends to a great extent on the

type of precursor, the amount and pH of the solution, since they greatly influence the formation of the active phase and its dispersion.

The catalysts present their active phase in the form of oxides dispersed in the support, but to present catalytic activity the oxides must be transformed into metal sulfides by an activation process. Activation consists of two steps: Reduction and sulfidation. The reduction by hydrogen allows obtaining vacancies in the catalyst. A fraction of Mo^{6+} is reduced to Mo^{4+} , while the rest is reduced to Mo^{5+} [27].

Sulfidation is the redistribution and transformation of inactive metal oxides into active metal sulfides with the appropriate geometrical configuration. Gas-phase sulfiding consists of passing a stream of H_2S/H_2 or C_2S/H_2 over the catalyst, however, this method is only performed on a laboratory scale. In industrial processes, sulfiding is carried out inside HDT reactors (in situ) with liquid feeds containing sulfiding agents, usually methyl disulfide as a hydrogen sulfide source agent. The reactions involved are described by equations (1) y (2).

$$9CoO + 8H_2S + H_2 \rightarrow Co_9S_8 + 9H_2O$$
 (1)
 $MoO_3 + 2H_2S + H_2 \rightarrow MoS_2 + 3H_2O$ (2)

2.4.3. Active Phase Models

In general, the mechanism of the HDS phenomenon is explained by the Solid-State Model [28], from which it follows that the fundamental transformations in HDS are:

- Adsorption (coordination) of the sulfur compound to the active site.
- Hydrogenation of unsaturated C=C bonds.
- Sulfur-carbon bond breakage (sequential or simultaneous).
- Addition of hydrogen to broken sulfur and carbon bonds.
- Exit of the hydrocarbon from the active site.
- Exit of H₂S from the active site.

The vacancies are sites where it can receive pairs of electrons donated by the sulfur atom, i.e., the vacancies result in chemisorption of the sulfur molecule on the catalyst. The vacancies are formed after the reduction step with H_2 . The mechanism of HDS with a thiophene molecule is presented in Figure 8. The thiophene molecule represents any sulfur molecule and X a vacancy.



Figure 8. HDS mechanism for thiophene explained by the vacancy model.

The active sites of the catalyst influence the activity and selectivity of the catalyst; however, their exact nature is still debated. The crystal structure of MoS_2 is the most accepted model for non-promoted Mo catalysts, which consists of S-Mo-S layers bound by van der Waals forces. Each unit cell consists of two S planes with an intermediate Mo plane, as shown in Figure 9. Each sulfur atom is bonded to 6 other sulfur atoms.



Figure 9. Structure of the crystalline phase of MoS₂. a) Lateral view of a layer. b) Top view of a block of MoS₂[17].

The crystals are located parallel to the basal plane (111) of the catalyst. Daage and Chianelli [29] demonstrated the existence of two types of sites in MoS_2 crystals. The Rim-Edge model describes the MoS_2 crystal as a stack of different disks (Figure 10). The top disks are the Rim sites where hydrogenolysis of the C-S bond occurs, although they can also occur at the Edge sites. However, hydrogenation occurs exclusively at the Rim sites.



Figure 10. Rim/Edge model of a MoS₂ catalytic particle [29]

On the other hand, bimetallic catalysts present the Co-Mo-S or Ni-Mo-S structure. The CoSx particles are located on the edges of the MoS₂ crystals. Two types of Co(Ni)-Mo-S structures are distinguished.

- Type I where Mo is not completely sulfided. This type occurs in conventional synthesis techniques and when the support has a strong interaction with the active phase.
- Type II where Mo is completely sulfurized, therefore, they are more active. It is obtained by increasing the calcination temperature or by a weak support-active phase interaction.

Figure 11 shows the different sulfur phases present in the $CoMo/Al_2O_3$ catalysts. The Co_9S_8 phase is due to a high Co/Mo ratio.



Figure 11. Sulfide species on the surface of CoMo/Al₂O₃ catalyst [17].

2.4.4. Hydrodesulfurization pathways

Currently, because most of the world's remaining crude oil reserves are heavy crude oil, more active catalysts are required for refractory compounds. Therefore, recent research has used 4,6-DMDBT as the main reactant. This compound presents steric hindrance because it has alkyl groups adjacent to the sulfur atom that hinder its removal by direct desulfurization. Possible routes that allow HDS have been put forward which are HYD and DDS. The hydrogenation route (HYD) consists of hydrogenation of the aromatic ring followed by removal of the sulfur atom. The direct desulfurization route DDS consists of the cleavage of the C-S bond, directly removing the sulfur atom (Figure 12) [30].



Figure 12. Hydrodesulfurization of DBT. DDS, direct desulfurization pathway; HYD, hydrogenation pathway [30].

2.4.5. Catalytic Deactivation

Deactivation results in loss of catalyst activity. These deactivations can be reversible or irreversible. Generally, in the case of reversible deactivation, catalytic processes in the industry have a catalyst regeneration stage which eliminates the carbon residues in the catalyst. On the other hand, irreversible deactivations make the catalytic converter unusable and must be replaced, generating costs to the company. Each type of catalytic converter has a useful life, which can be reduced by chemical, thermal or mechanical mechanisms. The deactivation phenomena can be grouped into:

- Poisoning: when certain molecules (poisons) are strongly chemisorbed on the active sites, reducing their number. Often, the poisons can be the reactants themselves, a product of the reaction or simply an impurity in the stream.
- Fouling: is due to the deposit of carbonaceous residues (coke) that are strongly adsorbed on the catalyst blocking active sites or pores leading to active sites. Coke can form multilayers where it blocks the access of reactants to the active sites.
- Sintering: This is due to the growth or agglomeration of metallic crystals. These crystals reduce the specific area and therefore the catalytic activity. This phenomenon is favored at high temperatures and accelerated in the presence of water vapor.
- Chemical degradation: This is due to the loss of the active centers of the solid catalyst due to its transformation, by chemical reaction, into volatile species. It has been reported that, due to the nature of the catalyst, the active phase can be redispersed giving rise to a new phase called inactive bulks.
- Mechanical failures: Due to the number of catalysts inside the reactor, they tend to deform underweight. The catalysts can fracture due to the thermal stress to which it is subjected, these fractures in turn can lead to erosion due to the continuous flow in the reactor.

2.4.6. Catalytic Regeneration

The main cause of catalyst deactivation is the accumulation of coke; therefore, catalysts must be regenerated since replacing them with new ones would result in higher costs and waste. Catalyst regeneration can be discarded when the active phase is contaminated by permanent poisons or very low catalytic activity, and by deficient physical properties such as mechanical resistance [31].

One of the most widely used methods for catalyst regeneration is Roto-Louvre oven technology. The process consists of analyzing various parameters such as residual carbon and sulfur, surface area, mechanical strength, poisons, to determine the operating conditions of the regenerator. The catalysts then enter the rotary oven, which uses hot air to initiate the combustion of sulfur and carbon. Finally, the catalysts pass to the screening stage where dust is removed and fine catalysts are eliminated to avoid pressure drop in the reactor.

2.5. Clays

Guggenheim and Martin (1995) define the term clay as "a natural material composed mainly of a fine-grained mineral, which is generally plastic at adequate water content and which hardens after drying or calcining" [32]. Clays have a particle size smaller than 2µm. When wet they possess sticky and plastic characteristics, however, when dry they are hard and cohesive [33]. Chemically, clay minerals are hydrated aluminum/magnesium silicates; they may contain other elements such as iron, calcium, sodium, potassium and others, with a lamellar or fibrous crystalline structure.

2.5.1. Origin

James Hutton developed the lithological cycle, which describes the formation processes and relationships that allow transformation between igneous, sedimentary or metamorphic rocks [34]. The model explains the transformation of rocks through time in a closed cycle. The rocks observed are in momentary equilibrium, because any change in their surroundings will break their equilibrium which will cause a transformation. To understand the origin of the various existing minerals, it is necessary to differentiate two very important layers, SIAL and SIMA.

The SIAL layer, located between 40 and 100 km deep in the Earth's crust, is rich in silica and aluminum, while the SIMA layer, located further inland, is rich in iron and magnesium with proportions of aluminum and silica [35]. After the cooling of the Earth's surface millions of years ago, the SIAL layer allowed the formation of igneous rocks and the SIMA layer gave rise to basic rocks. The first rocks were subjected to the harsh atmospheric conditions of that time, which after both physical and chemical processes resulted in several formations of various minerals.

Today, after millions of years of constant change, 95% of the Earth's crust is made up of silicates and part of these silicates are clays. According to Besoain [36], clays can be formed by inheritance, transformation and neoformation. Formation by inheritance indicates that mineral A is transformed into mineral B by the contribution or elimination of some elements,

conserving a large part of the original crystalline matrix. The other two mechanisms suggest the formation of clays during a chemical reaction, either synthesis from component elements or an original clay. Generally, clays from volcanic ash soils and alluvial volcanic sediments are formed from chemical and physical weathering resulting in the fragmentation of larger minerals to their characteristic size of less than 2 μ m, as well as an accumulation of oxides in their structure.

The physical and chemical properties of the resulting minerals depend on the characteristics of their source rock and the various processes to which it was subjected. As explained above, clays are often formed from soils with volcanic ashes, however, time and the composition of these ashes form a certain type of clay. A clear example is the formation of kaolinites and montmorillonites.

On the one hand, kaolinites are formed from feldspars of recent volcanic ashes, although isolated cases have been found of formations in ancient soils of ashes and pyroclastic material. This transformation occurs by weathering processes. Another mechanism proposed is the formation of montmorillonite or chlorite by desliming and desilicification. On the other hand, smectics are formed from volcanic ash deposits together with an abundance of basic cations and a high silica/alumina ratio. The formation of montmorillonite is favored in humid conditions, indicating that certain conditions influence the formation of one or the other type of clay [36].

2.5.2. Structure

Clay layers present a molecular structure based on the stacking of layers formed by tetrahedral and octahedral sheets arranged in different combinations (Figure 13) [37]. The tetrahedral sheet is composed of silicon and oxygen tetrahedra, which are bonded together by sharing three of their four oxygens. These oxygens are called basal oxygens and are in coordination with two silicon atoms belonging to two neighboring tetrahedra, forming a hexagonal pattern. Generally, the tetrahedral cations are Si and Al [38] [39]. The octahedral sheet is formed by magnesia or alumina octahedra. This octahedron is electrically unbalanced due to the negative charges contributed by the vertices, and to neutralize each other the vertices tend to share [39].



Figure 13. Clay structure. a) octahedral sheet and b) tetrahedral sheet [37]

The layer tends to have an excess of negative charge due to substitutions of some cations by others of lower charge. This effect is neutralized by the individual cations (usually Na^+ , K^+ , Mg^{2+}) existing in the interlamellar space. On the other hand, these cations can be in coordination with hydroxyl groups, forming an octahedral sheet. This type of configuration is called 2:1:1 layer, where the lamellar octahedral layer does not share vertices with the tetrahedral.

Depending on the combinations of the layers, two types can be distinguished. A 1:1 layer if there is an octahedral and a tetrahedral layer, while a 2:1 layer if there is an octahedral layer between two opposing tetrahedral layers [40]. The fourth oxygen of the tetrahedron is called the apical oxygen, which forms a bonding plane between the octahedral and tetrahedral layer, however, there are apical octahedral oxygen atoms that are not bound to any tetrahedron. These oxygen atoms bind hydrogen atoms to compensate their charge, forming hydroxyl groups [39].

2.5.3. Types

In nature, several types of clays are found, each one with different physical and chemical properties. This difference is mainly due to the arrangement and compositions of octahedral and tetrahedral sheets. Layer silicate minerals can be classified basis of these characteristics, structural characteristics, linkage configuration, chemical characteristics (net layer charge), and chemical character [41].

Family	Group	Subgroup	Specie	Formula	
		Kaolinite	Nacrite, Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	
1.1	Kaolinite-Sementine	Kaolinite	Dickite, Halloysite	Al ₂ Si ₂ O ₅ (OH) ₄	
1.1	Ruomite Serpentine	Serpentine	Antigorite, Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	
		Serpentine	Amesite	(Mg ₂ Al) (Si Al) O ₅ (OH) ₄	
	Pyrophyllite-Talc	Pyrophyllite	Pyrophyllite	$Al_2 Si_4 O_{10} (OH)_2$	
	i yiopiiyine Tae	Talc	Talc	$Mg_3 Si_4 O_{10} (OH)_2$	
			Montmorillonite	$(Mg_{0.33}Al_{1.67})Si_4O_{10}(OH)_2\cdotX^{+}_{0.33}$	
		Montmorillonite	Beidellite	$Al_2 (Si_{3.67} Al_{0.33}) O_{10} (OH)_2 \cdot X^+_{0.33}$	
	Smectite		Nontronite	$Fe_{2} (Si_{3.67} Al_{0.33}) O_{10} (OH)_{2} \cdot X^{+}_{0.33}$	
	2.1	Saponite	Saponite	$Mg_3(Si_{3.67}Al_{0.33})O_{10}(OH)_2\cdotX^+_{0.33}$	
			Hectorite	$(Mg_{2.67}Li_{0.33})Si_4O_{10}(OH)_2\cdotX^{+}_{0.33}$	
2.1			Sauconite	$(Mg_2 Zn) O_{10} (OH)_2 \cdot X^+_{0.33}$	
2.1	Vermiculite	Dioctahedral		$(A1 \ Fe^{+2})_2 (Si_{3.2} \ Al_{0.33}) \ O_{10} (OH)_2 \ Mg_{0.4}$	
		Trioctahedral		$Mg_3(Si_{3.2}Al_{0.33})O_{10}(OH)_2Mg_{0.4}$	
	Mica	Dioctahedral	Muscovite, Illite	$Al_2 (Si_{3.2} Al_{0.33}) O_{10}(OH)_2 K_{0.8}$	
		Trioctahedral	Biotite, Lepidolite	Mg ₃ (Si ₃ Al) O ₁₀ (OH) ₂ K	
	Chlorite	Di, Tri	Several proposed names	(Mg, Fe) ₃ (Si, Al) ₄ O ₁₀ (OH) ₂	
		Mixed	several proposed names		
	Paligorskite-Seniolite	Dioctahedral	Palygorskite	Mg Al ₃ Si ₈ O ₂₀ (OH) ₃ (OH2) ₄ \cdot 4H ₂ O	
		Trioctahedral	Sepiolite	$Mg_8 Si_{12} O_{30} (OH)_6 (OH2)_4 \cdot 6H_2O$	

Table 7. Classification of phyllosilicates related to clay minerals [41].

Among the most representative groups are kaolinite, smectite and palygorskite, and sepiolite. Kaolinite is an important industrial clay mineral in agroindustry, paper industry, and civil construction industry. Its chemical composition is Al₂Si₂O₅(OH)₄, which influences a low cation exchange capacity. Due to low cation substitution, it has a low surface area. Other remarkable characteristics are its low absorption capacity and low viscosity [42].

Smectite are very useful clay minerals in the catalytic industry and absorption process. Na⁺, Ca²⁺, Mg²⁺, Fe²⁺ and Li-Al cations are located in the space between the 2:1 layer. This type has high layer charge and high exchange capacity. Smectite has high absorption capacity due to its high surface area. Palygorskite and sepiolite are Mg-Al silicate materials. Both are very similar, only differing in the large unit-cell. This type has colloidal properties as the resistance to the high concentration of electrolytes. The surface area, absorption capacity and viscosity are relatively high [37].

2.5.4. Applications

Heavy metals are generally toxic to humans, even at low concentrations and because they are bioaccumulative. The most common heavy metals found in trace amounts are Fe, Mn, As, Pb, Se, Cu, Zn, Ni, Cd, Hg and Cr. The increase in the concentration of these metals is due to human activities, mainly industry, agriculture and mining waste disposal. In this context, several investigations have leaned towards the use of clays and pillared clays due to a more economically profitable process [43] [44] [45], thus concluding that clays can be used as natural adsorbents for heavy metal removal in aqueous systems.

Volatile organic compound (VOC) molecules such as methane, ethane, hydrogen sulfide and sulfur dioxide are released into the environment from industrial activity and natural sources. These VOCs react with other atmospheric pollutants such as nitrogen oxides to produce tropospheric ozone, contributing to the formation of photochemical smog and the greenhouse effect. Moreover, compounds such as benzene, vinyl chloride and 1,2-dichloroethane are extremely hazardous to health. Among the materials used in the adsorption of VOCs is activated carbon, although it has some disadvantages such as flammability, pore clog, hygroscopicity [46]. For this reason, alternative adsorbent materials such as clays have been promoted, mainly due to their adsorption capacity, high mass transfer rates, low cost, abundance and regeneration. For example, Nunes [47] made

chemical modifications to natural clays using cationic surfactants, then used it as an adsorbent for a bis(triethoxysilyl)benzene and tetraethyl orthosilicate mixture, and the results are very promising.

Pillared clays due to their pore size, acid sites and thermal stability have been often used as catalysts or catalyst support for catalytic reactions. Luck [48] compared different supports for catalysts, the results showed low HDS activities for clays attributed to their low surface area. However, the author suggests that in the future they can be used due to their low cost, high ease of synthesis, high mechanical strength. Álvez et al. [49] studied Ni, W, Ni-W catalysts supported on pillared clays. The results reveal that they are active on thiophene HDS, however, the Ni-W catalyst shows higher activity, probably due to the formation of active complexes. The author suggests that future studies should focus on increasing the specific surface area of the NiW/PAI catalyst. Recently, the use of clays for cosmetic and medical purposes has increased due to applications such as facial, hair and skin treatment and dental creams. Nonetheless, for such applications it is required that the clays have low or no toxicity [50].

2.6. Pillared Clays

Pillaring is the process by which lamellar composites are transformed into stable microporous and/or mesoporous materials with retention of the layer structure. A pillaring derivative is distinguished from an ordinary interlayer by the intracrystalline porosity made possible by the lateral separation of the interlayer host [51]. Calcination of the resulting expanded material leads to the conversion of the polycations into stable metal oxides, which can be considered as pillars that permanently keep the clay layers separated at a larger interlayer distance [52].

Pillaring agents are chemical species, which are introduced into the lamellar space to form pillars that induce porosity in the structure. Pillaring agents form metal oxide pillars that increase the thermal and hydrothermal stability of the clay [53]. Mostly, the pillaring agents used are hydroxication agents, such as Al, Zr, Cr, Fe, and so on [54]; nowadays mixed pillars are also used: Al-Fe [55] [56], Al-Cr [57] [58], Al-Ce [59]. The properties of pillared clays depend greatly on the cations used for pillaring. Pillared alumina clays are predominantly microporous, while clays pillared with titanium and gallium exhibit mesoporous, in addition to the thermal stability of 850°C [60]. Chromium

is commonly used for pillaring due to its oxidation numbers and relative acidity, however, Cr-PILC does not overcome the calcination phase, decreasing its surface area [58].

2.6.1. Preparation methods

Generally, smectite-type clays are preferred for catalytic material due to their textural characteristics. In the context of pillaring, they are appreciated for their high cation exchange capacity. The first step consists of slowly adding the pillaring agent to the suspended clays over a long period of agitation. The pillaring solution contains polyoxocation which replaces the inorganic cations in the interlayers of the clays. This impregnation increases the basal space up to 5 times. Control of pH, temperature and aging time are crucial in this step. Large amounts of pure water are consumed in this step due to the number of times it is repeated [61]. Finally, the solids are calcined to transform the hydroxide pillars to stable pillars. After pillaring formation, the material acquires the porous network and high surface area ranging from 230 m²/g [62] to 510 m²/g [63]. Figure 14 represents a schematic of the pillar formation process and shows the size ratio of the basal space. the decrease of the basal space (d₂) is due to the bonds changing from ionic to covalent increasing considerably the thermal stability [64].



Figure 14. Schematic representation of the pillaring process [64].

The process described above is called the conventional method. In the industrial field, using this method is unfeasible since it requires large amounts of water and heat, in

addition to high heat demand. For this reason, the study of microwave and ultrasound methods have been more relevant since these methods drastically reduce the preparation time and the amount of water required.

Intercalation step time can take just a few minutes using ultrasound. The procedure consists of subjecting the mixture of the pillaring solution and suspended clays to ultrasound around 20 to 30 minutes. Katdare et al. [65] prepared pillared clays and analyzed the effect of ultrasonic pretreatment time. The structural characteristics of PILCs prepared with ultrasound were slightly superior to those prepared with the conventional method. However, the time was significantly reduced. It is inferred that ultrasound accelerates the diffusion of Al13 polyoxication within the clay, while cation exchange occurs subsequent to the intercalation step. In the same way, Moma et al. [66] point out a substantial decrease in prepared by Moma show an increase in surface area and basal space, as well as high thermal stability.

Microwave irradiation was applied to synthesis of pillared clays, achieving excellent results in time reduction and with larger surface area than PILCs prepared with the conventional method, and thus large-scale fabrication is very promising [67]. Fetter et al. [68] studied the time course of exposure of clays to microwave irradiation. XRD patterns showed that only samples exposed between 10 and 30 min have well defined diffraction (001) peaks. Sassi et al. [55] used Al-Fe pillared montmorillonite as catalysts in catalytic wet air oxidation. The materials were submitted to 5 min to microwave irradiation and catalytic activity was compared with the conventional method. The results showed that both methods present similar catalytic performance, although, the catalytic deactivation was hindered in these catalysts due to well pore size.

2.6.2. Pillared clays in catalyst

Kloprogre et al. [69] prepared Nickel catalysts using Na-montmorillonite from Wyoming, which was pillared with Al₁₃. These materials were air- or freeze-dried and calcinated at temperatures between 473 and 973 K. The catalytic activity was tested by thiophene conversion measurement. The HDS activity of catalysts prepared from pillared clays shows higher activity than carbon-supported and alumina-supported catalysts. The authors explain that HDS activity may be due to a low metal-support interaction, which is directly proportional to temperature increases. A second explanation is a better dispersion of active sites; the active phase can be properly dispersed in a larger surface area. A third factor that influences HDS activity is the acidity, increase the temperature calcination minimizes the acidity of the clay due to loss of protons released from the pillars.

Ramos-Galvan et al. [70] prepared NiMo catalysts supported on Al- and Ti-PILC. Montmorillonite type clays from Durango, Mexico, were pillared with Al- and Tipolyoxocations. Then, the materials were dried at a temperature between 40-120 °C for 16 h and calcined at 300 and 500 °C for 2 and 3 h. The active phase Ni-Mo was impregnated using ammonium heptamolybdate and nickel nitrate. The XRD results display a drop in the concentration of the exchangeable cations, which is due to the displacement of the original cations by the polyoxocations intercalated upon the pillaring. The interlayer distance of Al- and Ti-PILCS were 17.7 and 18.6 A respectively. The overall HDS rate of NiMo/Ti-PILC was 24.8% HDS/m², which is a value higher than 9.7% for NiMo/Al₂O₃. Furthermore, upon the regeneration treatment, NiMo/Ti-PILC raises its overall conversion rate. It may be explaining by the redispersion of the active metals on the surface. The redispersion contributes to the formation of metal mixed phases, small crystallites of NiS and MoS, which enhanced the HDS catalytic activity.

Sychev et al. [71] prepared chromia-pillared clay and used them as catalysts for hydrodesulfurization of thiophene. Oglanlinsky montmorillonite was pillared with hydroxychromium polycations at 368 K for 36 h. The material was air dried at room temperature and heat-treated in a thin-bed with He flow. Sulfuration was performed with H₂S/He flow at 673 K for 2 h. The catalytic activity was measured in HDS processes at 623 and 673 K for 24 h. The catalysts were found to have a very low catalytic activity, with a thiophene conversion equal to 20%. Among the main reasons for their low performance is that the catalyst deactivated in the first 5 to 35 min of the test, such deactivation is attributed to the formation of coke. The products obtained show selectivity towards n-butane, indicating that the Cr-sulfide species are probably active for HYD.

Hayashi et al. [63] synthesized Co-smectites catalysts. Several types of smectites were used, including montmorillonite, saponite, porous saponite, hectorite and stevensite from Kunimine Kogyo. Co-smectite catalysts were prepared by a cation exchange method with cobalt nitrate solution and Co-porous saponite by incipient wetness method at 10, 20 wt.% of catalyst. The catalysts underwent presulfiding by flowing a gaseous mixture

of 95% hydrogen and 5% H₂S for 2h at 400 °C, then thiophene was injected and its conversion was measured with an on-line gas chromatograph. Cobalt porous saponite catalysts by cation exchange showed the highest performance among the prepared catalysts. At temperatures between 250 and 300 °C, these catalysts show even higher performance than the CoMo-Al₂O₃ catalyst (Table 8). On the other hand, Co-porous saponites did not show the desired activity. The high activity of these catalysts is due to the impregnation method used, which allows a good dispersion of Co over a considerably high surface area (510 m²/g). The temperature-programmed sulfidation (TPS) profiles showed H₂S consumption over a temperature range between 250 - 600 °C, indicating that the cobalt oxide is slowly sulfided and that the oxides are highly dispersed in the catalyst. Another factor is the effect of the positive charge of the cobalt oxides, which were formed after calcination of the impregnated Co cations from cation exchange. The temperature programmed reduction (TPR) profiles show a decrease in the reduction temperature, which allows the hydrogen molecules to dissociate at a lower temperature, benefiting catalyst performance. The resulting hydrocarbons were butane, 1-butene and 1,3butadiene along with a minimal amount of shorter chain hydrocarbons. This indicates that the catalysts are selective to HDS, but not to hydrocracking.

Table 8. HDS activity	y of Co-porous sa	aponite catalysts	prepared by	y various n	nethods [63]	١.

Catalyst sample	Loaded cobalt as oxide (wt%)	Thiophene conversion (%) ^a			
		250°C	275°C	300°C	
Co-porous saponite	7.7	73.5	81.8	92.7	
Co-porous saponite([*]) ^b	10.0	6.9	10.3	13.2	
Co-porous saponite(*) ^b	20.0	4.2	7.3	9.8	
CoMo-Al ₂ O ₃	Co: 4; Mo: 15	59.2	72.6	85.0	

^aCalculated from unreacted thiophene peak area of GC.

^bCobalt was loaded on porous saponite with incipient wetness method.

Salerno et al. [72] researched the effects on the pH of the impregnation solution in Mo supported on Al-PILC catalysts. Montmorillonite from La Serrata de Nijar (Spain) was pillared with Al₁₃ Keggin cation. It was obtained a basal spacing $d_{001} = 1.8$ nm. Molybdenum was impregnated by incipient wetness impregnation with (NH₄)₆Mo₇O₂₄·4H₂O solution at different media and pHs. After that, the materials were calcinated at 673 K for 4 h. The TPR profiles display two peaks of reduction between 780 and 1015, which indicate the reduction of Mo⁶⁺ to Mo⁴⁺ and Mo⁴⁺ to Mo⁰ species, respectively. The broad and asymmetric peaks at low temperatures provide an idea of the existence of polymeric Mo species and a small particle of bulk MoO₃. On the other hand, the broad peaks at high temperatures are attributed to isolate molybdate species formed with residual cations of the support. At acidic pHs, there is a preferential formation of bulk MoO₃ over polymeric Mo. On the contrary, at basic pHs, the formation of polymeric Mo is higher than bulk MoO₃. N₂ adsorption indicated that the pore size of Mo(10)/Loc was reduced concerning Al-PILC. This reduction is since Mo species are dispersed even within pillared clay. The order of catalytic activities was Mo(8.5)/Loc > Mo(10)/Loc > Mo(6.5)/Loc > Mo(4)/Loc (Figure 15). The highest activity of Mo(8.5)/Loc is attributed to the impregnation medium (H₂O₂) which allowed a homogeneous dispersion of the active phase on the clay. Additionally, highly dispersed MoO₃ microcrystals were confirmed by XRD and Raman. The difference between activities is attributed to the impregnation pH which influences the formation and dispersion of Mo species.



Figure 15. Comparison of the HDS activity for the catalysts at 643 K [72].

Salerno et al. [73] studied the effects of co-impregnation and sequential impregnation method on NiMo hydrotreating catalysts supported on Al-pillared montmorillonite. The NiMo/Loc catalysts were prepared by the co-impregnation method with a bimetallic solution. The Ni-Mo/Loc and Mo-Ni/Loc were prepared by sequential impregnation exchanging the metals' order of impregnation. The content was adjusted to 12 wt.% MoO₃ and/or 3 wt.% NiO. The HDS and HDN activities were obtained after 12 hours of reaction at different temperatures (Figure 16). The Ni/Loc catalyst showed null activity because most Ni species exchanged ions with the clay, in addition to low reducibility and sulphidability. The Mo/Loc showed low activity for HDS and null for HDN. This may be due to large MoO₃ crystals and incomplete desulfurization; however, it is balanced by a large number of acid sites in the catalyst. The Mo-Ni/Loc catalysts exhibit high activity for HDN and low activity for HDS. The activity presented in this

catalyst may be due only to the MoS₂ activity since it is unlikely that Ni-Mo-S active phase has formed on the catalyst. In contrast, Ni-Mo/Loc shows high HDS and HDN activity. Unlike Mo-Ni/Loc catalyst, it shows Ni-Mo-O active phase, probably formed after second-step impregnation with Ni, which promotes Mo phase redispersion. The highest activity obtained is the NiMo/Loc catalyst for both HDS and HDN, slightly higher than Ni-Mo/Loc. The activity is due to Ni-Mo-O phase formation attributed to the high dispersion of Mo species and that Ni was located at nearby sites. It was also found that the catalysts HDS/HDN selectivity, which is attributed to the deactivation of Brønsted acid sites.



Figure 16. Effect of catalyst preparation on the catalytic activity. a) HDS and b) HDN at different reaction temperatures [73].

Colin et al. [74] compared the hydrogenation activity of Mo supported on aluminium-pillared clay (Al-PILC) and zirconium-pillared clay (Zr-PILC). Montmorillonite type clays from La Encantada Co. (Mexico) was used as initial support for Al and Zr pillaring after molybdenum was impregnated by incipient wetness method. The MoS₂ catalysts activity was tested in HYD of naphthalene reaction. The activity order is MoS_2/Zr -PILC > MoS_2/Al -PILC $\approx MoS_2/Al_2O_3$. Colin et al. suggest that the differences in activities could be due to an effect induced by the presence of zirconium oxide on the small sulfide particles. The XRD results display large oxide particles, which were located on the external surface, near the pillars and the external sheets. Upon activation process, molybdenum atoms are linked to the support by Mo-S-Zr bounds promoting a complete sulfidation of small MoS₂ clusters, so it contributes to higher HYD activity.

Sugioka et al. [75] studied HDS activity and performance for thiophene in noble metals (Rh, Pt, Pd, Ru) supported on aluminum-pillared clays as of montmorillonite, hectorite, and saponite. The HDS thiophene activity was carried out in a conventional fixed/bed flow reactor at 350 °C and 1 atm. Rh/Al-PILM (montmorillonite), Pt/Al-PILH (hectorite) and Rh/Al-PILS (saponite) showed higher activity than CoMo/Al₂O₃. Besides, hydrocarbon products were mainly C4 hydrocarbons, which indicates that the catalysts are selective for HDS but have low activity in hydrocracking.

Iwasa et al [76] used synthetic smectite clay as HDS catalyst. The clay was synthesized using the hydrothermal method at pH 13.0; Si-Co hydrous oxide precipitate and aqueous sodium hydroxide solution were mixed; the resulting solution was filtered and dried. The XRD patterns indicate that the synthesized material shows small fragments with the smectite structure and there is no ordered arrangement like natural smectite-type clay. The surface area of the synthetic smectites was 300 m²/g, this is because the silicate fragments were possibly stacked in such a way that after calcination, they formed pillared structures. The catalysts presented high activity for HDS of thiophene and benzothiophene with a fixed-bed flow reactor at atmospheric pressure, which is due to the cobalt species located on the edge of the silicate fragments acting as active sites. These catalysts were shown to possess better activity than commercial CoMo/Al₂O₃ catalysts.

Hossain et al. [77] studied the thiophene HDS activity in Co-HPS (high porous) catalysts promoted by noble metal. The clay used was saponite from Kunimine Kogyo Co. Ltd, Japan. The Co was impregnated by ion-exchange technique, the noble metal was added by direct impregnation method in a load range of 0.1 to 2 wt.% of the catalyst. Then, the materials were dried at 120 °C followed by calcination at 600 °C. The elemental analysis shows a decrease in Co content, which may be due to the occupation of ion-exchange sites by noble metals. The TPR profiles display a decrease in the reduction temperature of the promoted catalysts concerning the initial Co-HPS catalyst, this effect is attributed to the noble metals dissociating the hydrogen molecules and allowing the cobalt oxide to be reduced at lower temperatures. The most noticeable effect occurs in the Co-Rh/HPS catalyst, the temperature decreases as the Rh loading increases (Figure 17), nonetheless, this occurs until the Rh reaches 1 wt.% content as it does not show substantial improvement beyond that value. As for the bimetallic catalysts, the Pt-Rh pair shows higher activity than the Pd-Rh pair, this can be explained by the XRD patterns where it is shown that the Pt dispersion was higher than Pd. The products after HDS were

mainly n-butane, indicating that the catalysts have high hydrogenation activity, and low hydrocracking activity.



Figure 17. TPR spectra of unpromoted and noble metal promoted Co/HPS [77].

Kanda et al. [78] investigated the effect of Pt precursor and pretreatment on HDS activity of Pt/AL-PILM catalysts. Several Pt precursors were impregnated on Al-PILM supports. The precursors were H₂PtCl₆·6H₂O), [Pt(NH₃)₄](NO₃)₂, [Pt(NH₃)₄]Cl₂·H₂O, H₂Pt(OH)₆. However, platinum (II) acetylacetonate (Pt(C₅H₇O₂)₂) was dissolved in toluene. The materials were uncalcined (UC) and calcined (C), after which were pretreated by reduction (R), sulfidation (S), TPR and TPS. Hydrodesulfurization of thiophene was performed at 350 °C under 0.1 MPa by a conventional fixed-bed flow reactor. The precursor Pt(C₅H₇O₂)₂ showed the highest activity over the others, even over commercial CoMo/Al₂O₃ catalysts (Table 9). This is probably due to the high dispersion of Pt particles on Al-PILM. The high dispersion was demonstrated by XRD patterns which showed barely visible Pt peaks, unlike H₂Pt(OH)₆ catalysts which showed large Pt peaks and their yield was the lowest. The UC-TPS Pt/Al-PILM catalyst was the catalyst with the highest activity, indicating that the pretreatment partially facilitates the formation of Pt sulfide species, thus achieving high dispersion.

Pt precursor	Thiophene conversion (%)					
	C-R	C–S	C-TPS	UC-TPR	UC-TPS	
$Pt(C_5H_7O_2)_2$	73.9	73.9	72.3	77.7	78.3	
$H_2PtCl_6 \cdot 6H_2O$	59.0	61.3	62.5	61.0	74.2	
[Pt(NH ₃) ₄](NO ₃) ₂	56.7	58.7	59.5	50.2	72.0	
$[Pt(NH_3)_4]Cl_2\cdotH_2O$	46.1	46.0	39.2	48.5	69.1	
H ₂ Pt(OH) ₆	12.9	6.4	10.2	10.9	11.8	

Table 9. Effect of pretreatment on HDS activities using different Pt precursors [78].

The effect of pH of the Mo impregnation solution on NiMo catalyst supported on pillared clays was studied by Rinaldi [79]. Montmorillonite from Sigma Aldrich was pillared with Al₁₃ Keggin cation type. Next, the materials were impregnated with Mo and NiMo aqueous solution, both at pH-1 and pH-10. The catalysts were characterized by XRD; the patterns display peaks of MoO₃ at pH-10 slightly lower than pH-1 which means a better dispersion around the support. The HDS activity by HDS reaction of Coker naphtha of NiMo/PILC pH-10, NiMo/PILC pH-1 and commercial NiMo catalysts was compared, with the result that clay-based catalysts are less active. Rinaldi suggests that low HDS is due to pH in the Mo impregnation solution is not adequate for considerably dispersion of Mo.

Due to the production cost of clay-based supports, it has been proposed to look for synthesis methods that allow them to be more viable industrially. Gao et al. [80] synthesized Al-pillared montmorillonite in situ. Montmorillonite used was extracted from Jilin in the Northwest of China. Al-(PEG)In-MMT was prepared by adding montmorillonite in a solution of AlCl₃·6H₂O in continuous stirring. Then PEG400 was added, followed by the NaOH solutions dropwise added. After washing 6 times with distilled water followed by centrifugation, the solid was dried at 60°C in the drying oven. Al-(No PEG)In-MMT was synthesized in the same way except that the PEG400 was no added. The XRD patterns display the basal spacing of Al-(PEG)In-MMT is 18.8 Å against 16.4 Å of Al-(No PEG)In-MMT. It was found that using PEG400 the surface area reaches higher values than by the conventional method, specifically the surface area of the raw montmorillonite is 20 m²/g, with the conventional method it reaches 144 m²/g, while the use of PEG400 allows reaching 182 m²/g. The nitrogen adsorption isotherms point out type IV isotherms and H4 hysteresis loop for materials, this indicates that Al-(PEG)In-MMT could be used as catalyst supporter.

An alternative to conventional methods for sulfur removal in refineries is oxidative desulfurization (ODS). Kang et al. [81] reported high ODS activities of molybdenum catalysts supported on Ti-pillared clays with cyclohexanone peroxide (CYHPO) as oxidant under mild conditions. The montmorillonite from Shangai Macklin Biochemical Co. Ltd. The Ti-PILC was impregnated with Mo and calcined at 500 °C for 3 h. The XRD patterns do not show the presence of crystalline MoO₃, indicating that it is probably highly dispersed on the support. Experiments showed that 0.100 g of catalyst reaches the maximum number of active sites available for CYPHO. The optimum oxidation temperature is 100 °C since at higher temperatures CYHPO starts to decompose. The optimum O/S molar ratio was 2.0 mol, the amount at which CYHPO has fully reacted with DBT. At the conditions described above, 30 min of reaction time is required to achieve a DBT conversion of 99.90%. In addition to the high activity, the Mo/Ti-PILC catalysts show high resistance to poison contamination and excellent performance after regeneration (Figure 18). The catalytic activity was almost unaffected after Mo/Ti-PILC was reused 9 times, which indicated that the catalyst presented excellent cycling performance in oxidation desulfurization of DBT.



Figure 18. Regenerated performances of the Mo/Ti-PILC on the conversion of DBT [81].

Lui et al. [82] prepared NiMoW-clay hybrid catalysts which exhibited higher HDS activities in dibenzothiophene (DBT). Na-based montmorillonite was modified by organic cations to increase interlayer spacing and ion exchange capacity. After, NiMoW was impregnated at different concentrations (24, 30, 42, 48% wt.) on modified clay calcined. The XRD patterns before and after the activation of the catalysts showed the transformation of NiMoW oxides in their sulfides respective, besides an improvement of the structural properties. The HDS activity increase along with the content of the active

phase until 99.8% of sulfur was removed at 42% wt. after that, the activity decrease. The improvements in surface area and pore volume in Na-montmorillonite promote a better dispersion of the active phase. On the other hand, the peaks at 111°C and 460°C in TPD profiles suggest that amount of acid sites also was enhanced which promotes in adsorption of DBT. Another remarkable factor is the catalytic stability of the NiMoW-OM catalyst; the activity was maintained at around 99.8% during the period of 168 h.

2.7. Clays in Ecuador

In the 1980s and 1990s, the cooperation between the German Federal Institute for Geosciences and Natural Resources (BGR) and the Ecuadorian Institute of Mining (INEMIN) made possible an inventory of Ecuador's non-metallic raw materials [83]. Due to the technology at that time, the data was not digitized and is still in the INEGEMM Documentation Center. For this reason, Uribe [84] made a summary of the inventory presented to make this information available to the academic and productive ceramic sectors of the country.

Uribe [84] focuses mainly on the use of clays as raw materials in the ceramic industry, manufacture of bricks, tiles, roof tiles, cement, among others. Among the clays identified are common clays, kaolinitic clays, smectite clays, halloysitic clays, and kaolinite, each of which has its characteristics and therefore a specific use. Table 10 shows a summary of their composition, origin and uses in the 80s and 90s.

Clays Minerals	Composition	Origin	Applications
Common clays	Impure primary clays, slime	Meteorization of granite schist	Bricks, tiles
Kaolinite clays	Quartz, kaolinite, illite, allophane	Meteorization of volcanic rocks	Ball clay substitute
Smectite clays	Montmorillonite, acid tuffs, tuffites, cristobalite, mica	Alteration of andesitic lavas	Red ceramic
Halloysite clays	Halloysite, allophane, feldspar, quartz	Meteorization of volcanic deposits	
Kaolin	Kaolinite	Feldspar decomposition	Ceramic industry, paper

Table 10. Clay minerals in Ecuador.

Currently, the highest concentration of clays is found in the Cuenca-Biblián-San Fernando and Loja-Malacatos-Catamayo intramountain basins; however, the largest production of clays is in the provinces of Guayas, Imbabura, and Morona Santiago. The clays extracted in these provinces are mainly due to the cement industry [85]. In Imbabura, Junín is the most important copper deposit in the country, and limestone is extracted in the surrounding area and used in the cement industry.

Kaolinite reserves have been identified in the provinces of Azuay, Cañar, Bolívar and Loja, which amount to 10 million tons; on the other hand, in the Cuenca-Biblián-San Fernando basins, 18.5 million tons are estimated. They are used in fine ceramics for the production of porcelain and earthenware, plastics, paints; however, their main use is as a coating pigment in the paper industry, about 45% of its production is used for this purpose [85].

Bentonites are rocks composed mainly of smectites. Bentonite deposits are found in the province of Santa Elena in the Tosagua Formation. In the Azogues Cuenca sedimentary basin, proven reserves are estimated at 500 thousand tons and 108 thousand tons of probable reserves. The San Cayetano Formation in the Loja-Malacatos-Catamayo basin also shows deposits of smectite clays [85].

Cruz [86] studied clayey sediments from the bottom of the Gulf of Guayaquil, Jambelí Channel and Guayas River. XRD analysis was performed on 75 sediment samples to identify the type of clays present. The average composition of the samples showed 90% montmorillonite, 9.5% kaolinite and 0.5% illite. On the other hand, Coronel [87] carried out an analysis of the clay minerals of the Jambelí Archipelago whose results show that 36% corresponds to illites, 35% to smectites and 29% to chlorites. Besides, it was found that the presence of saltwater does not alter the clays. These analyses indicate a distribution profile of clays along the Gulf of Guayaquil attributed to the types of soils carried by the rivers. Smectites and kaolinites predominate in the center and north of the Gulf, while illites predominate in the south.

Morales-Carrera [88] performed an analysis of clays from a field located in Guayaquil, belonging to the Ancon Group. The Ancon Group outcrops mainly in the Ancon Basin, south of the Chongon-Colonche Depression. The associated genesis corresponds to the neoformation of ashes from Andean volcanism. Specifically, clays belonging to the Clay Pebbe Bed Member of the Socorro Formation were analyzed. X- ray diffraction showed that they are dioctahedral smectite-type clays, in addition to small amounts of quartz considered impurity. The clay minerals are illite, kaolinite and mainly montmorillonite. The exchangeable cations were quantified where sodium, magnesium, potassium and mainly calcium were found, concluding that the clay is calcic bentonitic. Finally, the results obtained after activation with sulfuric acid suggest the use of these clays in the field of edible and industrial oil purification.

Valarezo [89] studied the clays of the San Cayetano formation located in the Loja Sedimentary Basin. The samples were subjected to X-ray diffraction where results showed a high quartz content can reach up to 60.09% in some places. Another mineral found in considerable proportions is montmorillonite reaching up to 30.92%. On the other hand, kaolinite reaches up to 34.06% in samples taken from the Palmeras neighborhood. Small proportions of minerals such as cristobalite, gibbsite, illite, pengite, hematite, among others, were found. Concerning to structural properties, figurines were made with each of the samples collected. The clays were treated, prepared and calcined at nominal temperature and the results obtained to comply with the required plasticity, shrinkage and density. Consequently, it was concluded that the clays are suitable for the manufacture of ceramics.

In the context of the use of clays as catalysts in Ecuador is very scarce, however, there have been investigations about the application in the field of adsorption. Lopez-Cordova et al. [90] synthesized LTA zeolites from clays with high Fe₂O₃ content to remove CO₂ with alkane-amine solutions. The clay samples were taken from the provinces of Bolivar, Cañar and Loja. The zeolites were synthesized using the alkaline fusion method. X-ray diffraction showed an increase in specific area and adsorption capacity after zeolite formation. The original clays have a specific area between 44 m²/g and 90 m²/g and CO2 adsorption values between 0.10 and 0.23 mmol CO₂/g. While the zeolitized clays showed surface areas between 105.2 m²/g and 390.2 m²/g, in addition to a CO₂ adsorption capacity between 1.31 and 1.93 mmol CO₂/g.

The textile industry plays a significant role in Ecuador's economy, as it is the second-largest manufacturing sector in terms of employment. Nevertheless, it is a major source of contaminated liquid effluents that affect color, pH, turbidity, and suspended solids in the water. This directly affects agriculture, livestock, and the health of people downstream. As a result, Obando [91] proposed the use of a mixture of quaternary salts

with clays as dye-reducing agents. Clays from Pujilí (Cotopaxi) and bentonites from Loja were used. The flow of water with dyes passed through a fixed bed of 3 cm thick clays for 3 h. The results show that the mixture of sulfur and dyestuffs in the clay was reduced by a mixture of sulfur and dyestuffs. The results show that the mixture of aluminum sulfate with bentonite and aluminum polychloride with black clay had the most favorable results in the reduction of dyes.

On the other hand, Perugachi [92] proposes the preparation of nanoclays from Ecuadorian coastal clays to use in the plastics industry. His study consisted of two parts, the first was to apply foreign nanoclays to Ecuadorian paints and the second to obtain Ecuadorian nanoclays. The paints modified with nanoclays showed a 50% increase in corrosion resistance, water vapor transmission up to 35% and water absorption up to 30%. Meanwhile, in the second part, the clays used were from the Ancon Group, which were modified with alkylammonium salts, so that the interbasal distance increased by up to 60%. Finally, although this type of technology brings advantages and can be one of the best investments in research, the plastics industry does not fully define the application of these materials.

CHAPTER IV

DISCUSSION

Oil is the primary source of energy, as well as a raw material for numerous processes in the chemical industry. In recent years, energy demand has increased, high oil prices and a decline in the production of light crude oil fields have boosted the exploitation of heavy crude oil fields. Seventy percent of the world's oil reserves correspond to heavy crude oil, extra-heavy crude oil and bitumen [8]. Generally, heavy oil fractions tend to contain higher concentrations of metals, heteroatoms and other elements. Therefore, the processing of these crudes involves exceptional efforts due to corrosion problems, transportation and mainly the deactivation of catalysts due to the effect of sulfur. From this point of view, in the coming years it is expected that the fields will produce crudes with higher levels of heavy metals and heteroatoms such as sulfur, nitrogen and oxygen.

Considering the increasingly stringent standards that regulate polluting emissions from fossil fuels, and the concern about environmental pollution, increasingly sophisticated sulfur removal methods have been proposed. The most widely used method is hydrodesulfurization, which is a process where most of the sulfur is removed from petroleum distillates using CoMo/Al₂O₃ catalysts. According to Maity [93] the initial catalytic activity is high, but it is quickly deactivated by coke and sulfur. Although after the regeneration stage the activity is similar to a fresh catalyst. Similarly, Ramos-Galván et al. [70] and Kang et al. [81] obtained excellent results after the regeneration stage. This phenomenon is explained by the redispersion of the active phase on the catalyst, in addition to the formation of small MoS crystals that improve the catalytic activity.

Although the pillared clays were synthesized for the purpose of catalytic cracking, they have been displaced by zeolite-supported catalysts. However, the unique characteristics of pillared clays make them ideal as catalytic materials for other reactions, especially in adsorption, where have been widely used [55] [57] [94]. Kurian & Kavitha [62] studied the effect of pillared clays and possible applications in green catalysis, focusing on their properties; is expected that the strategic design and preparation of clay-based catalysts can be targeted at the catalytic conversion of biomass-based and biomass-derived feedstocks.. On the other hand, Gil et al [95] reviewed the properties and applications of pillar clays and other layered materials used as catalysts, focusing on the

acidity of pyramidal clays and the effect on catalytic performance of using clays as supports for catalytically active phases.

Previous studies have shown that the catalytic activity of catalysts supported on pillared clays is very promising in the context of hydrodesulfurization [69] [71] [79] [96], since in most cases the characteristics of zeolites have been reached and/or surpassed. Consequently, it is necessary to discuss about significant parameters in the preparation of catalysts, related to the challenge of achieving more active and resistant catalysts. It should be emphasized that all the catalytic activity results are compared with CoMo/Al₂O₃ catalysts since they are the most used in hydrotreating processes.

Firstly, the montmorillonite type of clay is by far the most widely used clay in catalyst supports due to its versatility of preparation, high cation exchange capacity, high degree of selectivity [97]. Clearly this assertion is reflected in a number of publications concerning the pillaring of montmorillonite with Al. However, in the context of hydrodesulfurization, Hayashi et al. [63] reported that co-porous saponite catalyst possesses higher HDS activity at low temperatures than catalysts supported on activated montmorillonite. Likewise, Hossain et al. [77] also reported high hydrodesulfurization activity in high porous saponite modified with noble metals, especially combinations with Rh. These results are contrasted with the work shown by Sugioka et al. [75], where they compare catalysts supported on montmorillonite are more favored than saponite after pillaring, thus justifying their preference.

Secondly, several transition metals have been used as catalysts, however, the most representative ones are chromium [71], molybdenum [74] [81], cobalt [63] [77], platinum [78], nickel [69], nickel molybdenum [70] [73] [79], and mixtures between ruthenium, rhodium, platinum, palladium [75] [98]. However, impregnating the catalyst with these metals does not guarantee that excellent catalytic activity will be obtained. Kanda et al. [78] indicate that factors such as precursor, pH and pretreatment of the catalyst are crucial in the formation of the active phase and its correct sulfidation, as well as its uniform dispersion on the support.

Thirdly, the impregnation method plays a decisive role. Salerno [73] shows the relationship between the impregnation method and its catalytic activity. He concludes that the ideal impregnation method is sequential impregnation, since it promotes a better

dispersion of the active phase over the catalyst and allows the formation of Ni-Mo-S. However, the pH of impregnation solution and precursor induces notable differences in the distribution and dispersion of the Mo species in the oxidic state of the catalysts. Therefore, it can be inferred that the co-impregnation method requires ideal precursors to achieve excellent results as demonstrated by Guo & Lu [99] on other types of catalysts. Besides that, Gao [80] proposes the preparation of supports for in situ synthesis catalysts in order to make them industrially viable. The results show that PEG400 enhanced in situ pillaring achieves higher surface area, however, these supports have not yet been used for HDS catalyst.

On the other hand, one of the most common methods for the formation of clays is the process of volcanic ash weathering, therefore, Ecuador being a country with intense volcanic activity and with the passing of time, clay deposits have been developed in almost all provinces. The main deposits are located in Cuenca-Biblián-San Fernando and Loja-Malacatos-Catamayo intramountain basins. Aguiar [85], Cruz [86], Morales et al. [88] clearly show that smectite and kaolinite clays are predominant, with few major illite deposits.

The industrial applications of clays are very extensive; however, in Ecuador they have only been used industrially in the production of fine ceramics and cement, which clearly indicates a great delay. c [89]. In recent years, several researches have focused on the preparation of nanoclays in search of finding applications to new markets. Perugachi [92] prepared nanoclays with samples from the Ancon Group, Santa Elena, focusing on possible uses in rheological control of paints, membranes, sensors and obtaining nanocomposites with polymers. Although the results are very promising, the industry does not have a clear idea of specific applications of these materials. On the other hand, research has been carried out concerning the use of clays as adsorbents of dyes from the textile industry [91].

CHAPTER V

CONCLUSION

4.1. Conclusion

This work provides a review of the application of PILC materials in catalyst supports for hydrotreating purposes, especially hydrodesulfurization. Most of the research to date has been carried out in the field of petroleum cracking and refining. For this application, the type, amount, and strength of surface acidity of the surface and the thermal and hydrothermal stability of PILCs are crucial.

It was found that PILCs show great potential in various applications, basically due to their unique properties such as surface acidity, porous structure, and active substrates. The impregnation of noble metals in PILCs shows a decrease in the reduction temperature, which allows the dissociation of hydrogen molecules at lower temperature, benefiting catalyst performance. On the other hand, precursors and impregnation methods of the active phase can have a significant influence on the activity of the catalyst.

For the replacement of commercial catalysts in catalytic processes by catalysts supported on PILCs, the price and reliability of the new PILC-based catalysts (deactivation, coke formation regeneration or substitution) will be important factors. Although the catalysts show promising results, preparation methods that reduce preparation time and costs have not yet been tested on an industrial scale, making it difficult to determine the feasibility of these catalysts.

The information about clays in Ecuador was synthesized, finding that the main deposits are located in Cuenca-Biblián-San Fernando, Loja-Malacatos-Catamayo intramountain basins, and Ancon Group in Santa Elena. Among the clays identified are kaolinitic clays, smectite clays, halloysitic clays, which are mainly used as raw material in the ceramic industry, for the manufacture of bricks, tiles, roofing tiles, cement, etc.

There are numerous applications of clays worldwide, and although this material is abundant in Ecuador, there has been little research on its use in different industrial areas, especially in the area of catalysis. Previous studies about the plasticity, shrinkage, density and textural properties of the clays in Ecuador show similar characteristics to the clays used in catalysis, which could be an indication to consider their use.

4.2. Suggestions for future work

Throughout this work, some aspects were detected that should be further investigated for the possible application of clays as catalysts. Some recommendations for further studies are given below:

- The abundance of clays in Ecuador is evident; however, information about the type of clay found at the national level is scarce. Due to the wide range of applications of clays in the industrial field, it is necessary to characterize and study the properties of the primary deposits.
- Although clay-supported catalysts show higher activity than commercial catalysts at the laboratory level, their application in industrial equipment has not been recorded, influencing its feasibility.
- Molybdenum catalysts promoted with noble metals such as Rh, Pt, Pd, Ru tend to have higher catalytic activity; nonetheless, costs tend to rise.

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