http://www.ejournalofscience.org

Clays as Catalysts in Petroleum Refining Industry

Eman A. Emam
Department of Petroleum Refining Eng. and Petrochemicals,
Faculty of Petroleum and Mining Eng., Suez University, Suez, Egypt

emamtah@yahoo.com

ABSTRACT

In the last century, catalysts became one of the most powerful tools in the petroleum refining industry. Clays are widely used as catalysts and catalyst supports for a quite broad range of processes. Clay catalysts have attracted much interest in catalytic application in petroleum refining industry. This review will focus on the using of clays and their modifications as catalysts and catalyst supports in the petroleum refining industry. Clays are used extensively for various processes such as catalytic cracking, hydrocracking, reforming, isomerization, hydrogenation, alkylation, etc. The most important clays used in the manufacture of catalysts are kaolin and montmorillonite. The largest use of kaolin is in catalyst substrates in the catalytic cracking of petroleum, in the matrix as catalysts of fluid catalytic cracking, synthetic of zeolite andalumina. Montmorillonites or acid-modified montmorillonites also have been used for numerous reactions. For example, the best clay base for pillaring is a high-swelling Na-montmorillonite. However, the interest on palygorskite and sepiolite clays is more recent, but their interesting application as catalyst supports.

Keywords: *Petroleum refinery; clay; clay-modified catalysts; acidic-clay; pillared-clay; kaolin; montmorillonite*

1. INTRODUCTION

Petroleum is an extremely complex mixture of hydrocarbon compounds, usually with minor amounts of nitrogen-, oxygen-, and sulfur-containing compounds as well as trace amounts of metal-containing compounds [1-3].In addition, the properties of petroleum vary widely and are not conducive to modern-day use. Thus, petroleum is not used in its raw state. A variety of processing steps are required to convert petroleum from its raw state to products that are usable in modern society [1,2].

The demand for high value petroleum products such as middle distillate, gasoline and lube oil is increasing, while the demand for low value products such as fuel oil and residua based products is decreasing. Therefore, maximizing of liquid products yield from various processes and valorization residues is of immediate attention to refiners. At the same time, environmental concerns have increased, resulting in more rigorous specifications for petroleum products, including fuel oils. These trends have emphasized the importance of processes that convert the heavier oil fractions into lighter and more valuable clean products [4]. A number of technologies have been developed over the years for residual oil upgrading, which include process that are based on the catalyst, carbon rejection and hydrogen addition routes [1-4]. Besides, petroleum products are the basic materials used for the manufacture of synthetic fibers for clothing and in plastics, paints, fertilizers, insecticides, soaps, and synthetic rubber. The uses of petroleum as a source of raw material in manufacturing are central to the functioning of modern industry [2].

In the last century, catalysts became one of the most powerful tools in the petroleum refining industry [2,4,5]. Global capacity data of catalytic processing units in petroleum refineries collected by Silvy [5] indicate that hydrotreating boasts the highest global capacity and fastest growth compared to other majorcatalytic processes such as fluid catalytic cracking (FCC), hydrocracking (HC), reforming, alkylation and isomerization [4,6]. Catalyst life depends on the rate of deactivation by coke and metal deposits and sintering of the active phases [2,4,7]. Information regarding the activity, selectivity and deactivation of the individual catalyst is, therefore, highly desirable for optimizing the catalyst systems.

Clays or clay-modified catalysts are commercially used catalysts [8-15]. Clays have extensive applications due to their swelling, adsorption and ion exchange properties and high surface areas [16].Starting from the beginning of petroleum refining and petrochemical industries, clays have been used as catalysts [1,2]. The first hydrocracking process developed over 80 years ago was based on acid-modified clays [9],but later and still now, zeolites and aluminosilicates were used. However, in few cases such as in treating some heavy fractions, clays are still used. Clays with different acidities can be obtained by thermal treatment before preparing the catalyst. The temperature of the thermal treatment of the clay determines the type and concentration of the hydroxyl groups [17], and thereby its acidity. Montmorillonites or acid-modified montmorillonites have been used for numerous reactions [10, 18-20]. The most important clay used in the manufacture of catalysts is kaolin and has many applications such as a catalyst substrates in the catalytic cracking of petroleum [10,13].Further, kaolin is used to synthesis zeolite [21-27] and alumina [28-32].The discovery of the possibility of modification of these clays by pillaring with metal-oxide or of intercalating between the sheet anions, complexes, and organic chemicals represented a breakdown in the catalytic chemistry of these materials, because introduced new possibilities in mastering the properties and reactivity, although not fully explored [9,33,34].

In general, clays are very versatile materials and hundreds of millions of tons currently find applications in

many industries as adsorbents, catalysts or catalyst supports, ion exchangers, etc., depending on their specific properties.This review will discuss the applied of clays as catalysts and catalyst supports in the petroleum refining industry.The discussion will include the different types of clays and clay-modified catalysts, which are the most relevant for catalysis. Clay-modified catalysts according to the different modification methods such as: thermal, acid and cation exchange, pillared clays were discussed. In addition, the synthetic catalysts from clays such as zeolites and alumina were explained. Additionally, the review focuses about the using of clays in the matrix as catalysts.

2. PETROLEUM REFINERY

Petroleum refineryis a complex system of multiple operations and the operations used at a given refinery depend upon the properties of the crude oil to be refined. There are numerous possible refinery configurations and each is designed to achieve the specific target of transforming crude oil into useful products such as liquid petroleum gas, gasoline, kerosene, diesel and a large number of other products that are used as raw material in the petrochemical industry [1,2,35]. Petrochemical plants are sometimes incorporated within the refinery complex.

All refineries have three primary sections: separation, conversion and finishing [1,36]. Figure 1 shows an overall flow diagram for the refinery processes [1]. The first step in any refinery is separation of the crude oil into component streams in a distillation unit. Distillation is used to separate the crude into different boiling-range fractions for efficient conversion and cleanup downstream. Modern conversion refineries typically have two distillation towers in series, a tower operating close to atmospheric pressure followed by a vacuum unit. The towers contain trays or structured packing for vapor-liquid contacting and heights of 45 m are common[36].

Conversion processes convert less useful fractions into those that are in greater demand. The most conversion units are catalytic cracking, hydrocracking and coking [1,36]. These units convert the high molecular weight oil fractions from separation into components that become finished products. Catalytic cracking is the premier conversion process found in the refinery. Nearly 20% of all distilled crude oil is proceeding in catalytic cracking unit.

Accordingly, fluid catalytic cracking (FCC) is a central technology in refining [37]. The FCC unit is used to upgrade heavy gas oils and resid fuels to gasoline, diesel fuel, and light gases. In the mid 1930's a search was made for catalysts which would increase the rate of the more desirable cracking reactions. The best catalysts so far known are certain clays, and synthetic materials consisting of silica and alumina [1,2]. The earlier cracking catalysts were clays sometimes modified with sulfuric or other mineral acids to increase their activity [13,38,39].

Another important refinery conversion process is hydrocracking (HC). HC combines breaking of carbon-carbon bonds with the addition of hydrogen. HC may take many forms depending on the application. HC is a catalytic process that converts heavy oils to lighter fractions primarily by means of aromatic saturation, cracking and isomerization reactions in the presence of hydrogen. Catalysts employed in HC reactors have multiple functions. First, the catalyst has a metallic component (cobalt, nickel, tungsten, vanadium, molybdenum, platinum, palladium, or a combination of these metals) responsible for the catalysis of the hydrogenation reactions [2]. The component responsible for the cracking promotes cracking reactions and isomerization reactions. The cracking function is typically provided by solid-acid components in the catalyst support. These acidic components usually are silica-alumina, acid-modified clays, acid-metal phosphates, or alumina responsible for the cracking reactions [1,2,36].

The last important refinery conversion process is coking. Coking deals with the heaviest part of the barrel those components with boiling points exceeding 540 °C known as vacuum resid. Unlike the majority of other refinery process steps, no catalyst is used in coking. Time and temperature are used to convert the vacuum resid by means of two reaction pathways thermal cracking and condensation.

Products from these conversion steps are then treated in several finishing steps to make them ready for sale. The most widely used process in the finishing steps is hydrotreating a generic name given to a wide range of hydrogenation or hydrogen-addition steps. The most common reason for using hydrotreating on any refinery stream is sulfur removal. In addition to removing a substantial amount of sulfur, hydrotreating may also target other compounds containing metals and nitrogen and occasionally olefins and aromatics may be hydrogenated.

The demand for ever-increasing volumes of high-quality motor gasoline has heightened the focus on molecular rearrangement processes reforming, alkylation and isomerization. This rearrangement is necessary because the gasoline boiling range streams from conversion and hydrotreating are rich in straight-chain paraffins and naphthenes that have low octane numbers. All of these processes are catalytic.

http://www.ejournalofscience.org

Fig 1: Typical refinery process flow showing separation, conversion and finishing sections with end products.

The products produced in all of the conversion and finishing steps are almost ready for sale. Straight-run products may need additional treating steps for drying and sulfur removal, and many products will require some blending and additives to meet final sales specifications. Depending on the location, gasoline usually requires

additives for oxidation, metals and corrosion inhibition plus anti-icing. Depending on the complexity and product requirements, some refineries may have units to produce asphalt, wax, lubricating oils and greases. In addition to

the major processes, there are other auxiliary activities that are critical to the operation in a refinery.

3. CLAYS

Clays are in general constituted essentially by minerals that are hydrous silicates of aluminum and/or magnesium, with significant amounts of iron, nickel, chromium and other cations in the crystalline structure as an isomorphic substitution [10,35]. The peculiar crystalline structure of some clay minerals generates a capacity of reversible exchange with organic or inorganic

cations and metal-organic [10,27,40]. The exchange of specific cations can generate active centers in the clay minerals, making them catalysts, which can be then used for a large number of chemical reactions in industries. The properties of clays, that make them useful as catalysts are (a) the crystalline structure, (b) the modification of the original crystalline structure in a controlled way (c) the anisometric morphology and small sizes of the particles quite adapted for use in catalysis and (d) the change of its basal spacing by acid treatment and subsequent modification [12]. Furthermore, in order to protect the environment, several sets of regulations have been established [9,41,42]. Owing to this legislation, great interest has been devoted to the substitution of unfriendly and corrosive liquids, used in chemical and petrochemical industries by solid catalysts. On this basis, clays may constitute very promising substitutes. The clays mostly used as catalysts are smectite, kaolin, halloysite, palygorskite and sepiolite [9,12,27].

3.1 Clay Structure

The physical-chemical properties of a particular clay mineral are dependent on its structure and composition. The behavior of the physical-chemical of clays has been studied because of its relation to the adsorbent and/or catalytic properties in the process industries [27]. This behaviour is governed by the extent and nature of their external surface, which can be modified by suitable methods such as acid- and thermal-modifications. Acid- and thermal-modifications increase the catalytic and adsorbent activity of certain clays, but further and stronger modifications decrease this activity [12,17]. They have significant potential in chemical processing.

The structure and composition of kaolins, smectites and palygorskite and sepiolite are very different. They are naturally occurring aluminosilicates having sheets structure. These are the SiO_4 tetrahedron and $Al(OH)_3$ gibbsite or $Mg(OH)_2$ brucite octahedral unit as shown in Fig. 2 [10]. Tetrahedral layers consist of continuous sheets of silica tetrahedra linked via three corners to form a hexagonal mesh and the fourth corner of each tetrahedron is shared with adjacent octahedral layers. Octahedral layer consists of flat layers of edge-sharing octahedra containing cations at its center [35]. The octahedral cations are normally Al^{3+}, Mg^{2+}, Fe^{2+} and Fe^{3+}, but other medium size cations of Li^+, V^{5+}, Ti^{4+}, Cr^{3+}, Mn^{4+}, Co^{3+}, Ni^{2+}, Cu^{2+} etc., also occur in some species. However, the arrangement and composition of these octahedral and tetrahedral sheets account for major and minor differences in the physical and chemical properties of kaolin, smectites and palygorskite [27]. Table 1 shows some of the properties of kaolin, smectite and palygorskite that account for many of their applications [10].

3.1.1 Kaolin

Kaolin is one of the more important industrial clay minerals, with the chemical composition $Al_2Si_2O_5(OH)_4$ [21,35]. As mentioned in Table 1, kaolin is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral. Because of this limited substitution in the kaolin layer, kaolin has a relatively low surface area and a low surface charge compared to smectites and palygorskite and sepiolite [27]. The most common kaolin mineral is kaolinite, which is a common clay mineral, but the relatively pure and commercially useable deposits are few in number. Kaolinite has physical-chemical properties which make it useful in a great number of applications. Kaolinite is less reactive when incorporated into most industrial formulations which accounts for many of its more important applications. Other kaolin minerals are dickite, nacrite, and halloysite. Dickite and nacrite are rather rare and usually are found mixed with kaolinite in deposits of hydrothermal origin. Relatively pure halloysite deposits are rare; one of the only commercial halloysite deposits now operating is located on the North Island of New Zealand [10].

3.1.2 Smectite

Smectite minerals are composed of two silica tetrahedral sheets with a central octahedral sheet and are designated as a 2:1 layer mineral (Table 1). Water molecules and cations occupy the space between the 2:1 layers. Smectite is the mineral name given to a group of Na, Ca, Mg, Fe, and Li-Al silicates [10]. The most smectite minerals commonly used are Na-montmorillonite, Ca-montmorillonite, saponite (Mg), nontronite(Fe), hectorite (Li) and beidellite (Al) [10,16,35,43]. Ca-montmorillonite is the most predominate of the smectite minerals and is found in many areas of the world. Na-montmorillonite is relatively rare in occurrence in comparison with Ca-montmorillonite. The smectites occur as extremely fine particles of the order of 0.5 µm or less. Smectites are the dominant component in bentonite, which is a rock term. The term bentonite was defined by Ross & Shannon (1926) as a clay altered from glassy igneous material, usually a tuff or volcanic ash. Grim &Guven (1978) redefined the term bentonite to be any smectite clay that does not include the mode of origin [10,27]. Bentonites which are used industrially predominantly comprise either Na-montmorillonite or Ca-montmorillonite and to a much lesser extent saponite and hectorite [27,35].

3.1.3 Palygorskite (Attapulgite) and Sepiolite

Palygorskite and attapulgite are synonymous terms for the same hydrated Mg-Al silicate material, with the chemical composition (Mg, Al)$_5$Si$_8$O$_{20}$(OH)$_2$(H$_2$O)$_4$.4H$_2$O [44]. The name specified by the International Nomenclature Committee is palygorskite. Sepiolite is structurally similar to palygorskite except that it has a slightly larger unit-cell. Both minerals consist of double silica tetrahedral chains linked together by octahedral oxygen and hydroxyl groups containing Al and Mg ions in a chainlike inverted structure. These inverted tetrahedral occur regularly and cause channels through the structure. Both palygorskite and sepiolite are elongate in habit [27]. The elongate shape of these two minerals results in unique colloidal

ARPN Journal of Science and Technology

properties, especially the resistance to high concentrations of electrolytes. The elongate particles vary in length from about 1 to 10 µm and are approximately 0.01 µm in diameter. This shape and size results in high surface area and high porosity when thermally activated [10].

3.2 Clay Applications

Natural clays are thermally inert and environmental friendly and possess various uses and applications. The important characteristics relating to the applications of clays are particle size and shape, surface chemistry, surface area, surface charge, and other properties specific to particular applications, including viscosity, colour, plasticity, dry and fired strength, absorption and adsorption, abrasion and pH [27,45]. In addition, the low cost of clay and its relative abundance in nature, high sorptive/electric charge properties, plus ion exchange ability and compatibility with several materials, gives it a wide range of applications [46,47].
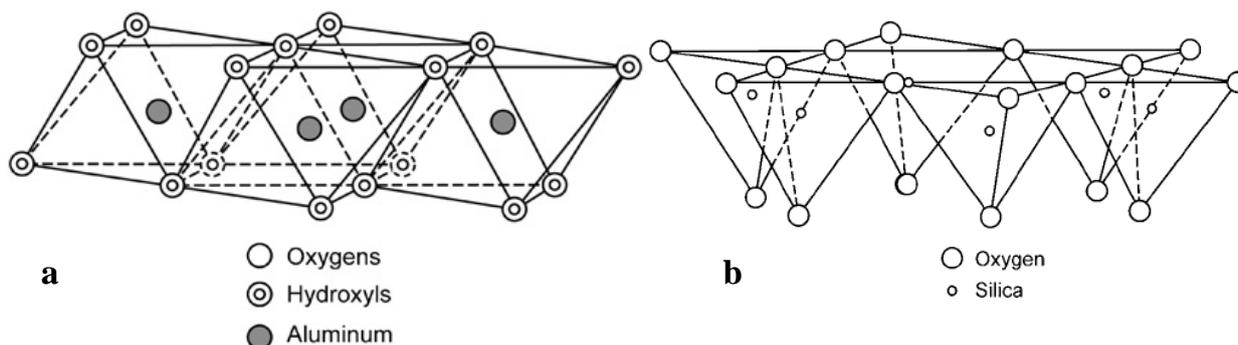
Fig 2: Clay structure: a. octahedral sheet and b. tetrahedral sheet.

Table 1 Some properties of clays

Kaolin	Smectite	Palygorskite
1:1 layer	2:1 layer	2:1 layer inverted
White or near white	Tan, olive green, white	Light tan
Little substitution	Octahedral and tetrahedral substitution	Octahedral substitution
Minimal layer charge	High layer charge	Moderate layer charge
Low base exchange capacity	High BEC	Moderate BEC
Pseudo-hexagonal flakes	Thin flakes and laths	Elongate
Low surface area	Very high surface area	High surface area
Very low absorption capacity	High absorption capacity	High absorption capacity
Low viscosity	Very high viscosity	High viscosity

The use of clays as catalysts has received considerable attention recently [10,12,15]. Also, the large surface area of the clay makes it a suitable support for other catalysts. Clays are widely used as catalysts and catalyst supports for a quite broad range of processes: catalytic cracking, hydrocracking, alkylation, isomerization, hydrogenation, reforming, ring opening, ethylation, denitrogination, dimerization esterification, polymerization, etc. [8,11,13]. Clays have been used as cracking catalysts particularly for heavy feedstocks and have also been explored in the demetallization and upgrading of heavy crude oil [2,48-51]. The results indicated that the catalyst prepared was mainly active toward demetallization and conversion of the heaviest fractions of crude oils. An emerging area of interest relates to the alcohol (methanol, ethanol) to olefins reaction. Other applications for which clays were patented include NOx abatement, Fischer-Tropsch reaction, cracking of waste plastics, selective oxidation, and synthesis of fine chemicals [9].

3.2.1 Kaolin

The most important clay used in the manufacture of catalysts is kaolin.Because many catalysts are used at high temperatures and pressures, the refractory character of kaolin is appropriate for many applications. For most industrial applications kaolin must be refined and processed from the crude state to enhance its whiteness, purity and other important commercial characteristics [27,35]. The largest use of kaolin is in catalyst substrates in the catalytic cracking of petroleum [10,13].The purity of the kaolin is critical in this petroleum cracking operation so processed kaolin with low iron, titanium and alkali and alkaline earth compounds is preferred. It is estimated that over 200,000 tons of kaolin are used annually to produce petroleum cracking catalysts [10].Kaolin is the most important raw material in a matrix with zeolite as a catalyst in FCC process[38,52,53], which kaolin clays modified the properties of catalytic cracking catalysts, such as reducing coke yield, improving attrition

resistance, high tolerance to contaminated metal and high thermal stability[13].Kaolins are quite good catalysts for Diels-Alders reactions [3]. They are also excellent supports for Lewis acids or for transition metals, to be applied in various organic reactions (Friedel-Crafts, acylation and alkylation of aromatics, etc.) [9].Depending on the metal, the Brönsted versus Lewis acidity can be tuned, allowing obtaining a family of catalysts [9,41,42].

Another application for kaolin is in the synthesis of zeolites [21-24,26].In addition, kaolin has been identified as a potential raw material for the production of alumina, one of the most widely used catalyst support material for hydrotreating[6,28,29,31,32].Kaolin and halloysite are used to make cracking catalysts, as a polymerizationcatalyst, peptide bond formation, and others [10].Halloysite and metakaolin are used in the manufacture of molecular sieves used as petroleum cracking catalysts. The kaolin for this application must be low in iron and in alkalies and alkaline earth elements. The dry surface of kaolin is very acidicand is used to promote the polymerization of styrene, heterolytic breakdown of organic peroxides, dehydration of alcohols, hydrolysis of esters,and isomerization of alkenes [10].

3.2.2 Smectite
In the mid-1930s, acid-modified smectite-type clays were widely used as commercial catalysts in petroleum-cracking reaction [18].Furthermore, pillaring of smectite clay minerals with inorganic cations are processed for use as catalysts in a number of reactions [10,19].Ca-montmorillonites are used in some processes involving the catalytic cracking of petroleum [20].Na-montmorillonite is used for the dehydration of oils. In general, montmorillonites or acid-modified montmorillonites have been used for many organic reactions such as the alkylation of phenols [54],the dimerization of a-methyl styrene and for many laboratory synthesis, for example, the preparation of di-2,2′-alkyl ethers [10]. Cation exchanged montmorillonites are also effective catalysts including Ni-montmorillonite for hydrogenation, Al- and Cr-montmorillonites for lactonization reactions, and Fe- and Co-montmorillonites to protonate several organic species [9]. Ion exchanged montmorillonites behave as solid acid catalysts and are effective and selective catalysts for the hydration of ethylene, aluminum exchanged montmorillonite was the most effective [55].Na-bentonite exchanged with cations of high charge density such as Al, Cu,Fe, and Cr is an efficient and selective catalyst for the production of ethylacetate from ethylene and acetic acid. There are many patents in the catalysis field using montmorillonites as the template.

3.2.3 Palygorskite and Sepiolite
The applications of palygorskite and sepiolite are as varied as those describedfor kaolins and smectites.Palygorskite and sepiolite clays are being used increasingly as catalyst supports on account of their high surface area, mechanical strength and thermal stability [10,56].Thecatalyst is readily available in systems because

it is not tightly held on thesurface of the palygorskite and thus is released.In the beginning of this century mainly the palygorskite clay was employed in isomerization, oxidation and polymerization reactions [57]. The catalyst can be impregnated on the surface by treatment with a salt of another metal and can also substitute for some structural Mg cations. Also, Mg^{2+} ions can be exchanged for catalytically significant species such as Ni^{2+}, Pt^{n+}, Pd^{n+}, Zn^{2+}, Co^{2+} and Cu^{2+}. Acid treatment of these clays results in the removal of adsorbed cations and impurities, increasing surface area, and altering the pore-size distribution and crystallinity. Heating above 300°C decreases the surface area but increases the strength of granules; this is significant to fluid-bed cracking [56].

4. CLAY-MODIFIED CATALYSTS
One of the problems of using clays as catalysts is that they deactivate at high temperatures due to structural collapse. In addition, clays may possess a low ability to catalyze reactions in either polar or non-polar media. Today a large spectrum of structural, textural and compositional modifications are possible for clays, allowing a fine-tuning and control of the catalytic reactivity [9,34,58,59].This makes these materials very interesting for catalytic applications.
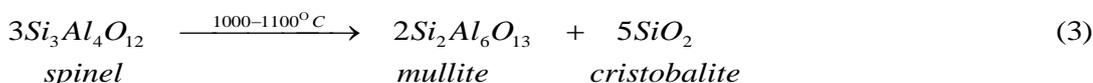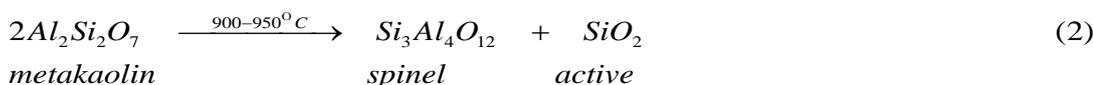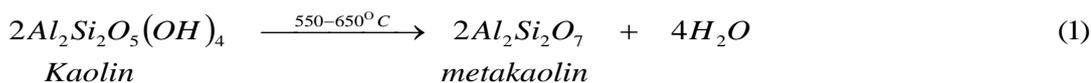
Various modifications of clays such as, thermal-, acid-, cation exchange, etc., alter the structure properties and produce catalysts with high acidity, surface area, porosity and thermal stability [16,43,58,59].Modifications can also be effected by impregnation of metal oxides such as vanadia, chromia, zirconia and alumina. Pillared clays are another modification in which the ions on the clays are exchanged with specific chemicals such as Al-hydroxide which goes into the interlayer position [27]. By controlling the amount of chemical added, pore sizes, specific absorbent and adsorbent characteristics, and unique catalytic properties can be regulated[60].Moreover, the introduction of silica alumina and synthetic zeolites might have slightly over shadowed the significance of clays in catalytic applications in petroleum refining. Nevertheless, clays retain their continuing importance as they constitute the matrix of manyindustrial catalysts based on zeolites. The claysmodification and its applications in petroleum refining processes are briefly described below.

4.1 Thermal-Modified Clays
Clay catalysts have been shown to contain both Brönsted and Lewis acid sites [3], with the Brönsted sites mainly associated with the interlamellar region and the Lewis sites mainly associated with edge sites. However, Brönsted acidity is mainly due to the dissociation of adsorbed water between the sheets. This dissociation is induced by the polarizing power of the cation (e.g., Al^{3+}, Fe^{3+}), which depends on the size and the charge of the ion. The clay acidity is very much influenced by the quantity of water between the sheets. Catalysts with different acidities can be obtained by thermal treatment before preparing the catalyst. The temperature of the thermal treatment of the clay determines the type and

http://www.ejournalofscience.org

concentration of the hydroxyl groups [17] and thereby its acidity.If the clay is heated (to around 100°C) so as to remove most of the interlamellar water until only one layer of water remains, at about 5% total water level, the Brönsted acidity increases markedly [60] to that of a very strong acid. Heating to a higher temperature (at around 200-300°C) results in the collapse of the clay interlayer structure as the water is driven out, resulting in a decrease in Brönsted acidity. The clay assumes a much more pronounced Lewis acid character, which is due to the transformation of Brönsted acidity into Lewis acidity.

Further heating (to around 450°C and above) results eventually in complete dehydroxylation of the aluminosilicate lattice, producing a completely amorphous solid that retains Lewis acidity [3].It was reported that there were several structural changes in kaolin during calcinations (thermal treatment) [39].For example, during calcinations kaolin undergoes the following reactions [61]:

$$2Al_2Si_2O_5(OH)_4 \xrightarrow{550-650^O C} 2Al_2Si_2O_7 + 4H_2O \qquad (1)$$
$$\textit{Kaolin} \qquad\qquad\qquad \textit{metakaolin}$$

$$2Al_2Si_2O_7 \xrightarrow{900-950^O C} Si_3Al_4O_{12} + SiO_2 \qquad (2)$$
$$\textit{metakaolin} \qquad\qquad \textit{spinel} \qquad \textit{active}$$

$$3Si_3Al_4O_{12} \xrightarrow{1000-1100^O C} 2Si_2Al_6O_{13} + 5SiO_2 \qquad (3)$$
$$\textit{spinel} \qquad\qquad \textit{mullite} \qquad \textit{cristobalite}$$

Uncalcined precursor microspheres of clays cannot convert to zeolite or alumina, which affect the crystallinity of them. To synthesize zeolite or alumina, the precursor microspheres must be calcined to form active SiO_2 and Al_2O_3. The results show that calcined microspheres of kaolin must possess better strength, high content of active alumina and silica and higher dissolving rate of alumina and silica. Calcined microspheres of kaolin have prerequisite of synthesis good quality zeolite.

Also, the effect of clays calcination depends on the type of layer silicate. In the case of octahedrally substituted clays (montmorillonite type), the protons will migrate into vacancies in the octahedral sheet, where they associate with lattice oxygens. In general, these protons are not accessible to catalysis, because the free of diameter of the hexagonal hole in the tetrahedral sheet is only 0.26 nm. After calcination the acidic sites left will be situated at the edges. However, for tetrahedrally substituted clays, calcination leads to protons attached to surface oxygens of the tetrahedral sheet. This results in acidic sites that are similar to the Brönsted acidic sites on Y-zeolite [62]. Plee et al. [63]worked with pillared montmorillonite and beidelliteand observed that the acidity of calcined beidellite compared well with Y-zeolite, while the calcined montrnorillonite-based catalyst was much less acidic. With 1R spectroscopy it was shown that on beidellite mainly Brönsted sites occurred, while montmorillonite exhibited a much lower acidity which was mainly of the Lewis type.

Rong and Xiaostudied the catalytic cracking activities of kaolin-group minerals (dickite, kaolinite and halloysite) catalysts after calcination at 200°C [13]. It was observed that the inter-layer water was removed completely, from kaolin-group minerals and their normal chemical compositions were nearly similar, namely $Al_4[Si_4O_{10}](OH)_8$, except for some impurities. Kaolin-group minerals have different catalytic cracking activity rates: the micro-reaction activity is: halloysite (24.3%)>kaolinite (13.4%)>dickite (about 0%) at 460°C (catalytic cracking temperature). The catalytic cracking activity of the kaolin-group minerals is not closely related to their chemical composition, but is mainly related to their mineral composition, which determined the activity of their hydroxyls. The catalytic cracking activity of the kaolin-group minerals may be mostly affected by their macro-structure (specific surface area, pore size and pore volume). Kaolin-composing of dickite, may be used as the no-activity matrix of catalytic cracking catalyst.

Herrero et al. [17] prepared heterogeneous catalysts by dehydrating palygorskite at 150°C or 400°C in vacuum, before the support and the hydrogenating species (rhodium) were put in contact. The heating and cooling pretreatment in vacuum allowed controlling the water content. This would not have been possible at atmospheric pressure because palygorskite adsorbs water reversibly, if it has been evacuated at 150°C and irreversibly if it has been evacuated at 400°C. These prepared catalysts were active in the hydrogenation of 1-hexene.

As mentioned above, thermal treatment influences the applications of clays incorporating with additional modifications. For example, thermal modified clay may be subsequent with acid-modified, etc., or subsequent with synthetic another materials such as zeolite or alumina. The applications of these catalysts will discuss in the following sections.

4.2 Acid-Modified and Cation Exchanged Clays

The acid-modified and cation exchanged clays can be simply regarded as solid acids and act as heterogeneous catalysts, with all of the advantages of easy removal of the catalyst from the product. Acid-modified clay is carried out by treating the clay with concentrated

http://www.ejournalofscience.org

mineral acids such as sulphuric, phosphoric and hydrochloric acids. This results in changes to surface area, porosity and the type and concentration of the ions in the exchange sites [8]. During acid modifications, Al^{3+} and Mg^{2+} cations are removed from the octahedral sites in the clay layers by the action of the acid and are relocated in the interlayer space where they act as acid centres. This promotes catalytic activity by increasing the number of Brönsted and potential Lewis acid sites. Also, on acid modification, some of the Al, Mg and Fe in the octahedral layer of the clay are dissolved out, leaving 'floppy' silica sheets. Folding of the sheets can form mesopores (100 Å) which are able to accommodate larger molecules for sorption and catalysis. The first catalysts used for catalytic cracking were acid-modified clays, formed into beads. In fact, clays are still employed as catalyst in some cracking processes [2]. In addition, the acid-modified clays have found particular applications in industrial processes such as isomerization [64], alkylation [65,66],polymerization of unsaturated hydrocarbons [40].

Cations exchanged such as Na, Ca, and Mg occur between the silicate layers, associated with water molecules. These elements are exchangeable and the property of exchange capacity is measured in terms of milliequivalents per 100 grams. The property of ion exchange and the exchange reaction are very important in many of the clay applications. For example, the cation exchange capacity of smectites ranges from about 40 in Ca-montmorillonite to 150 milliequivalents in hectorite per 100 grams. Na-montmorillonite has an exchange capacity which generally is between 80 and 110[10].The surface properties of clays can be also modified by exchange interlayer cations and water layers by polar organic molecules such as alkylammoniumions [40], ethylene glycol, quaternary amines and polyalcohols [27]. This is an important property which can be translated into some very useful organo-clay products [27,40]. The alkylammonium ions hold the aluminosilicate sheets permanently apart and increase the interlamellar spacing and expose new sorption sites on the clays [40].
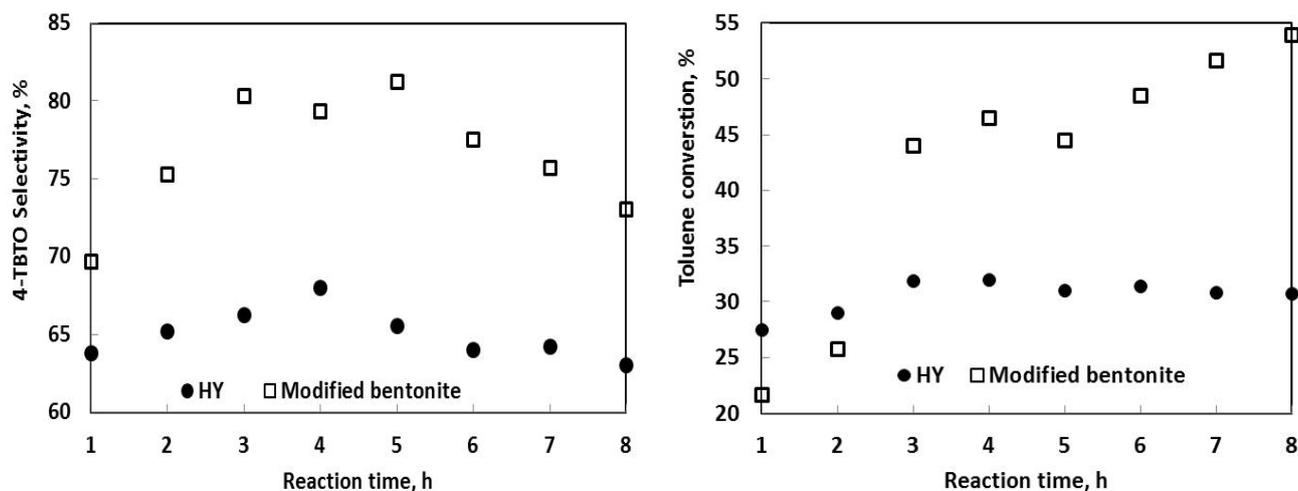
The combination of acid-modification and cation exchanged intercalation provides a potential enhancement of the clay properties. In the first instance, the clay is hydrogen-saturated by cation exchange in acid solution, resulting in a proton rich environment when presented to organic molecules. In the second instance, the catalytic abilities can be further improved by providing organic cations in the interlamellar space, which permit access to and interact effectively with organic molecules. The possibilities for catalysis in these systems are therefore much greater because both the internal and the external surfaces are available for reaction[40].

The clay most widely used as an efficient solid acid catalyst was montmorillonite for a number of reactions and offer several advantages over classic acids: strong acidity, non-corrosivity, cheapness, mild reaction conditions, high yield and selectivity, ease of set up and work up, possess comparatively strong acid sites and partly amorphous nature provides mesoporosity over a wide range of pore sizes [8,66]. The acid-modified montmorillonites find diverse applications as catalysts, catalytic support and adsorbents [65].The acid-modified montmorillonite catalysts are widely studied in petroleum cracking [2] and for many organic reactions [9] such as isomerization [64], alkylation [66]and acylation [67] reactions. Also, conversion of methanol to alkanes and of synthesis-gas to hydrocarbons has also been achieved [3].

Linbo and Li investigated and compared the effect of reaction conditions on catalytic activity and selectivity ofthe alkylation of toluene with tert-butanol over acid-modified bentonite and HY zeolite catalysts [65]. The catalytic activity tests were performed in a fixed-bed tubular micro-reactor equipped with flow controllers and a heating system. The optimal results were obtained at a reaction temperature of 180°C, a space velocity of 4 h^{-1}, and a mole ratio of toluene to tert-butanol equating to 2. The structure and acidic properties of catalyst were characterized by BET and Fourier transform infrared (FT-IR) spectroscopy. Compared with the HY zeolite, the acid-modified bentonite possessed high activity for toluene conversion and high para-selectivity 4-tert-butyltoluene (4-TBTO) because it had larger pore diameter, smaller micropore surface area and higher ratio of total Lewis acids to total Brönsted acids (Fig. 3).

Sun et al. [39] investigated the properties and reaction performance of catalyst additive made from acid-modified kaolin microspheres for gasoline sulfur reduction in FCC using mini-fixed fluid bed reactor. Sample characterizationN_2 adsorption, IR acid characterization, X-ray diffraction and reaction studies. After calcination and acid leaching, a certain expedite active pore structure was formed in the kaolin microspheres. Additive made from the modified microspheres exhibited improved coke selectivity and yield distribution. Incorporation of 15% of the additive into the base catalyst gave 18% gasoline sulfur reduction.

Fig 3: 4-*tert*-butyltoluene selectivityandtoluene conversion on modified bentonite and HY zeolite catalysts

.

Many applications of acid-modified and cation exchanged clays can be incorporating with another modification. For example, acid-modified clay is incorporating or impregnated with another metal. In addition, the catalytic behaviour of pillared clays is usually associated with the acidity modification. The discussions of these applications are in the following sections.

4.3 Metals Modified/İmpregnated Clays

Many conventional catalysts applied in petroleum refining industry are derived from oxides of an element belonging to group VIB (Mo or W) or group VIII (Ni or Co) supported or impregnated on different material as alumina, clay, etc. [48,49]. The structure, the composition of the metal oxide and the extent to which they interact with the clay support may all influence the catalytic activity of the parent clay material. Impregnation also modifies the acidity, due to varying dispersion and interaction with the oxide surface and contributes to conversion and selectivity. For example, the catalyst base, such as acid-modified clay, usually supplies the cracking function that is used to support the hydrogenation function supplied by metals, such as nickel, tungsten, platinum, and palladium. It has been assumed that the addition of the noble metal introduces a better balance between the acidic function (for cracking) and hydrogenation function of the catalysts, which helps reducing the gaseous product formation by suppressing the over cracking of heavy hydrocarbon molecules [68]. This characteristic of a hydroprocessing catalyst is of great importance for its industrial application since deep cracking produces lighter gas, which is considered as waste. In addition, noble metals have been considered to hold promise minimizing coke deposition on hydroprocessing catalysts [49]. These highly acid catalysts are very sensitive to nitrogen compounds in the feed, which break down the conditions of reaction to give ammonia and neutralize the acid sites. As many heavy gas oils contain substantial amounts of nitrogen (up to approximately 2500 ppm) a purification stage is frequently required. Denitrogenation and desulfurization can be carried out using supported cobalt-molybdenum or nickel-cobalt-molybdenum [2].

Also, the metals demonstrated excellent promotional effects in both activity and stability in some supported metal catalysts applied in different reaction systems, such a steam/dry reforming of methane and naphtha reforming [69]. Usually, a trace of the metals is used because of the rare availability and the high cost [70].On the other hand, highly efficient modern bi-metallic naphtha reforming catalysts owe their success to metal promotion.

The success of bi-metallic naphtha reforming catalyst has encouraged researchers to apply the same concept to hydroprocessing catalysts in an attempt to enhance catalyst activity, stability, and also to prevent coke deposition [49].

Many authors investigated the preparation of the heavy oil upgrading catalysts from different oxide metals supported on different clays [48-51]. Aoki et al. [50] showed that mesoporous smectite-like materials supporting cobalt can exhibit high activity of thiophene hydrodesulfurization (HDS). Arai et al. [51] also reported similar results in supported Co-smectite clay catalysts. Clay (saponite, smectite, etc.) was used as support in place of alumina. The smectite clay materials such as high porous saponite (HPS), saponite, hectorite, stevensite have not been extensively investigated as support for heavy oil upgrading catalysts despite their high surface area and favorable pore structure. However, Kimura et al. [71]reported highly active Co/HPS catalyst. The catalyst was tested in a batch autoclave reactor using vacuum gas oil as feedstock. But, the coke formation on such catalysts was also reported to be high. Therefore, the enhancement

of the catalyst stability was left as a challenge for the success of such catalyst. Ali et al. [69] also reported that the noble metal could significantly improve the catalytic activity of a high surface area saponite supported Co catalyst for hydrocracking (HC) and HDS processes of vacuum gas oil in a batch autoclave reactor.

Several authors were compared the HDS and HC activities of bi-noble metal promoted Co-clay catalysts [48,49,70,72]. The presence of noble metals influenced to improve the stability of the Co-clay catalyst for longer period of time during hydrotreating of vacuum gas oil. The coke deposition of the catalyst was significantly reduced due to the noble metals effects. Also, Hossain elucidated the promotional effects of trace amount of noble metal (Rh, Pd, Pt) on Co-saponite clay catalysts by using different characterization techniques [70]. Various catalyst characterization methods showed the active

element/phase and the influence of various factors on the active phase generation. The catalytic performance of the noble metal promotion catalysts were tested with the HDS and HC activities in a batch autoclave reactor at 400°C using vacuum gas oil as feedstock, which is the real feed in a heavy oil hydrotreating unit. The results showed that the introduction of noble metal leads to a higher catalytic activity and reduced carbon deposition on the catalyst. Furthermore, all of the noble metal promoted catalysts exhibited higher HDS and HC activities as compared to the unpromoted Co-saponite and among those the Rh promoted catalyst provides superior performances (Fig. 4a and b). These superior activities were attributed to enhanced reducibility and metal dispersion of cobalt due to the
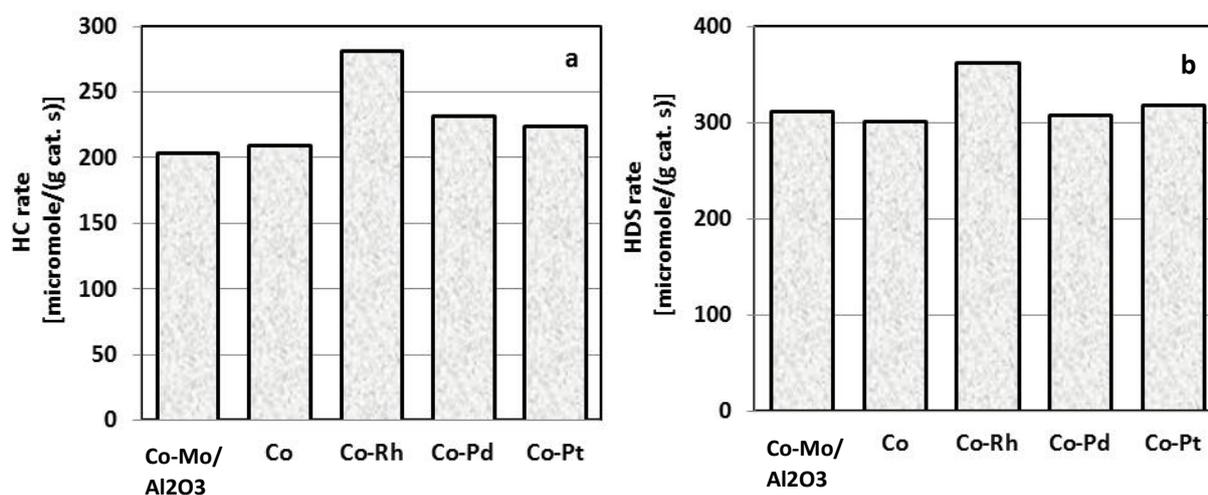
Fig 4: (a) HC and (b) HDS activities comparison of noble metal unpromoted/promoted Co-saponite and Co-Mo/Al$_2$O$_3$ (reference catalyst)

influence of the noble metals. However, both HC and HDS activity of Co-clay was significantly increased when thecatalysts were modified with a trace amount of Pt-Rh [49,72]. Also, it has been explained that the noble metals are very effective in generating a sufficient amount of reactive hydrogen, which prevents coke deposition by reacting with the cracked reaction intermediates [69,72]. Moreover, Hossain et al. [49] investigated of the promotional effects of the noble metal Pd, Rh on the catalytic activity of Co on the high porous saponite (HPS) support catalysts for heavy oil upgrading using a batch autoclave reactor for both HDS and HC activity test. Both the HC and HDS activity of noble metal-promoted on the high porous saponite support catalysts were found to be higher than that of plain Co/HPS catalysts. The coke deposition on Pd-Rh promoted catalyst was also found lower than that of the plain and single noble metal promoted Co/HPS.

Riad et al. [73]investigated the effect of the type of supports either kaolinite and or bentonite (lamellar

structure) aluminosilicate clay materials on the pore structure of prepared, calcined and reduced Pt-Sn catalyst. The catalysts were characterized by X-ray diffraction pattern, temperature programmed reduction and nitrogen physisorption technique to determine the BET surface area and the pore size distribution. The activity of catalysts was measured toward n-pentane isomerization reaction in pulse micro-catalytic reactor operated under atmospheric pressure and at temperature range 200-450 °C. The results indicate that supported Pt-Sn is more active towards iso-pentane formation than Pt catalysts. Meanwhile, Pt-Sn supported on kaolinite is more selective to iso-pentane formation (57.6%) than that supported on bentonite (38.0%).

Choudhury and Misra prepared Pt (II) clays, Cu (II) clays, acid clay and sol-gel hybrid materials of Cu (II) clay as solid catalysts using montmorillonite KSF by suitably adjusting their acidity and surface area by acid modification [8]. Friedel-Craft alkylation of benzyl chloride with toluene over the various clay catalysts using

365

differential scanning calorimeter (DSC) was performed. The authors concluded that the acidity and dispersion of solid catalyst are two important factors which influence reaction rates and activation energies of a chemical reaction. Among the catalysts used, acid Pt (II) clay and Pt (II) clay dispersed by natural dispersant are shown to be more effective catalysts due to more number of acidic sites and better dispersion of clay platelets. The major advantage of clay as solid catalysts is its good activity as well as its easy removal from the reaction mixture. Moreover, the catalysts are environmental friendly as they prevent hazardous wastes from environment. The activation energies turn over frequency (TOF) and reaction rates of various clay catalysts employed for Friedel-Craft alkylation reaction of benzyl chloride with toluene was reported in Table 2.

Melo et al. reported that the palygorskite clay containing terbium (TB^{3+}) [74] and lanthanum (La) [44] by ion exchange does not change the catalyst structure, albeit leading to an increase in the surface area and generation of Lewis acid sites. In addition, the TB^{3+} and La support palygorskite clays showed very good activity for isopropyl alcohol dehydration.

Table 2: Activation energies, rate of reactions, order of reactions and TOF of clay catalysts

Catalyst names	E_a (kJ/mol)	$L_n(K_0)$ (S^{-1})	N	TOF (S^{-1})
T703-15	608.6	181.31	0.85	0.18
T704-4	133	39.94	0.88	0.5
T704-1	133	39.94	0.88	0.5
T704-2	212.2	66.97	1.03	0.45
T704-3	308.75	94.36	1.03	0.3
T606-11	555.65	180.9	1.12	0.2
T606-12	509.2	167.92	1.2	0.25
T606-14	1673.19	500.64	1.49	0.15
T606-15	1694.79	519.82	0.82	0.13

Where:
- T703-15: montmorillonite clay,
- T704-4: Pt (II) clay,
- T704-1: acid Pt (II) clay,
- T704-2: Pt (II) clay where clay is dispersed by natural dispersant,
- T704-3: Pt (II) clay where clay is dispersed by cetyltrimethyl ammonium bromide (CTAB),
- T606-11: Cu (II) clay where clay is dispersed by natural dispersant,
- T606-12: Cu (II) clay where clay is dispersed by CTAB and
- T606-14 and T606-15: sol-gel materials of Cu (II) clays.

4.4 Pillared Clays

Pillared clays (PILCs) are one of the promising porous materials which can be utilized as catalysts in a number of reactions. More than thirty years have passed since the first announcement of pillared interlayered clay.The preparative techniques have progressed remarkably with a wide variety of pillared solids being made. Recent advances in the synthesis of PILCs have

expanded considerably the scope of their potential catalytic applications [18,58,75,76]. PILCs are formed by intercalation of polymeric metal hydroxides or oligomerichydroxycations into the interlamellar space of the cationic clays, followed by thermal treatment, allows pillaringof the clays, with a modification of the interlayer distance and typically also an increase of the thermal stability [9,75,76]. The catalytic behaviour of PILCs is usually associated to the modification of the acidity (by substituting tetrahedral and octahedral sites), by active sites introduced during the pillaring process and by intercalation with organometallic complexes. The method of pillaring could largely affect the final characteristics and performances [58]. Also anionic clays could be pillared [77]. These materials, particularly those having isopoly- and heteropoly-anions intercalated between the layers, show a quite interesting catalytic behavior [9]. Moreover, the transition metal oxide pillars can be modified by oxidation/reduction to become catalytically active and the pillars of the clay create specific and stable active sites. In these contexts first row transition metals like iron, titanium, vanadium and chromium-pillared materials are mostly studied. So there is enough scope of developing new catalytic materials for different applications by varying the transition metal oxide pillars only. This area of research is still growing and need further exploration as potential catalyst which is very limited in the literature. Generally, it is also claimed that the pillaring procedure significantly improves the performances with respect to the starting clays. As a result there is now a renewed interest in the pillared material as polyfunctional catalysts and catalyst supports [18,76].

Several research groups have investigated the characteristics of PILCs and their use as catalysts or catalytic materials [9,34,58,75,76]. The general conclusion which may be derived from thesestudies that pillared clays are very interesting and promising catalysts in a broad range of applications, for example in acid-catalyzed reaction [9], catalytic hydrotreating of heavy vacuum gas oil[78], alkylation of aromatics [79], the synthesis of bulk and fine chemicals (a broad range of reactions such as dehydrogenation, hydroxylation, disproportionation, esterification, epoxidation, alkylation, isomerization, Fischer-Tropsch, methane reforming, hydrogenation, aromatization, etc.) [34,58], upgrading of lubricant oils and for the reduction of pollutants (selective catalytic reduction of NOx and catalytic removal of organic volatile compounds [9]).

The best clay base for pillaring is a high-swelling Na-montmorillonite [16,80,81].It is mineral clay that can hold guest molecules between its layers. Many different cations, including hydroxy-aluminium, hydroxy-chromium, hydroxy-titanium and hydroxy-zirconium polycations have been used for the preparation of pillared montmorillonite characterised by surface area of 200-400m^2/g, pore volume of 0.15-0.30 cm^3/g and interlayer spacing of 1-2 nm [80]. Vaughan and Lussier demonstrated that montmorillonite interlayered with hydroxy-aluminium pillars will promote catalytic

ARPN Journal of Science and Technology

cracking and hydrocracking [81]. Infrared spectra of adsorbed pyridine showed that both Brönsted and Lewis acid sites are present on the surface of the pillared clays. It was showed that the Brönsted acidity and the catalytic properties of Al-pillared montmorillonite could be improved by acid modification of the clay prior to its pillaring[80].Several studies on catalytic cracking are based on Al, Ga and Si-pillared clays. In some cases transition oxide-pillared clays are also studied for cracking reaction[18]. Cr-pillared laponite prepared using microwave irradiation is found to be a good catalyst for hydrocracking of heavy liquid fuels. Catalyst is found to be active even after 4 h of reaction regardless of high coke formation. The same catalyst can be reused without any decrease in the activity [78]. Also, it was reported that by incorporating Al into Cr-PILC, both the thermal stability and surface acidity for the final mixed Al/Cr-PILC were improved, resulting in a higher activity in the catalytic cracking of cumene [18].

Sulfide pillared clays can be produced by combining clay with metal sulfides.The modification of the metal oxide pillars by electronegative ions like sulfates, results in the production of strongly acid components, where the inductive effect of the S=O group increases the charge in the neighbor metal cation (M^+) [82]. A variety of techniques has been reported in the literature aimed on the way to introduce SO_4^{-2} ions on the metal oxide surfaces. Among them, are the impregnations with $(NH_4)_2SO_4$ or H_2SO_4 solutions as well as treatments with SO_3, SO_2 or H_2S followed by oxidation [80]. Many data concerning metal sulfides supported on pillared clays have been reported.Iron sulfide-pillared montmorillonite was first prepared by Burch and Warburton to be used for high-pressure demetallization to remove nickel and vanadium from heavy crude oil; however, the product obtained was highly interstratified [76].Issaadi et al. [80] showed that contact reactions of hexanes on 1 wt% Pd/alumina pillared acid-modified montmorillonite and 1 wt% Pd/sulphated zirconium pillared sodium montmorillonite exhibit much better activities and isomerization selectivities compared to those obtained on conventional pillared montmorillonite.

Various catalysts have been proposed as hydrodesulfurization (HDS)and hydrocracking (HC) catalysts [69,76,83-85]. In HDS and HC, transition metal sulfides catalysts supported on PILCs, possess some properties comparable to those of the zeolites, silica-alumina or alumina [76,83]. Their pore structure and catalytic behavior can be varied over a wide range by changing the type of intercalate. Kloprogge et al. [85] demonstrated that montmorillonite can be impregnated with nickel followed by sulfidation to provide catalysts exhibiting comparable and even higher thiophene HDS activities than alumina- and carbon-supported nickel sulfide catalysts. The catalytic activity increased by raising the amount of Al13 pillars from 5.5 meq Al/g to 20 meq Al/g, whereas an increase in calcination

temperature results in an activity loss. 5.5 meq Al/g is sufficient to saturate the montmorillonite.

Also, it was found thatchromium sulfide-pillared clay is a suitable catalyst for HDS thiophene [16]. However, Cr-pillared montmorillonite exhibits high activity and selectivity in cyclohexane dehydrogenation, hydrocracking of *n*-decane and toluene disproportionation, as well as dehydrogenating properties in cumene conversion. Cr-pillared clay modified with an H_2S-H_2 mixture displayed interestingly high activity for thiophene HDS and consecutive hydrogenation of butane [76]. The catalytic activities of noble metals (NM= Pt, Pd, Rh, Ru) supported on Al-pillared montmorillonite clay(Al-PILM) were examined at 350°C and compared with various carriers such as metal oxides, carbons, zeolite and mesoporous silica for HDS of thiophene as a model HDS reaction for petroleum in a conventional fixed bed flow reactor under 1atm [84]. The order of catalytic activity of NM/Al-PILM was Rh/Al-PILM >Pt/Al-PILM >Pd/Al-PILM >>Ru/Al-PILM and this activities were comparable to that of CoMo/Al_2O_3 as shown in Fig.5. However, it was revealed that sulfided Rh supported on SiO_2, amorphous carbon,Pt supported on HZSM-5, MCM-41 and Rh supported on Al-PILM showed high and stable activities for the HDS of thiophene. The activities of these catalysts were higher than that of commercial CoMo/Al_2O_3 HDS catalyst.
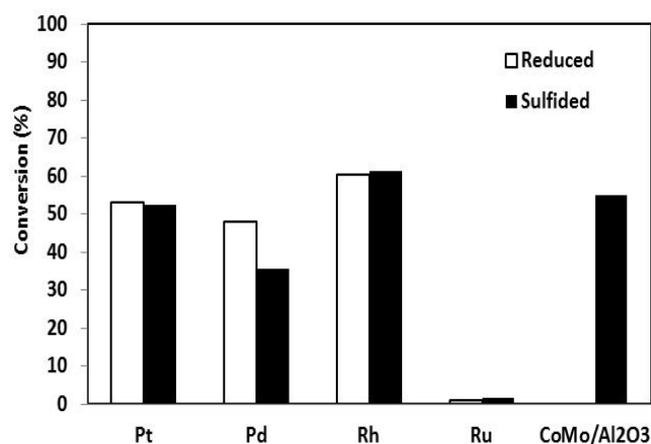

Fig 5: Catalytic activities of noble metals supported on Al-PILM for the HDS of thiophene.

Sychev et al. synthesized Cr-pillared clay from naturally occurring montmorillonite through exchange of interlamellar ions with hydroxyl-chromium polycations [76] and from Li-montmorillonite calcined in a controlled manner [86]. The catalytic activities and stabilities of the catalystswere examined at 400°C for HDS of thiophene. The heat treatment of Cr-pillared clay under the conditions applied did not drastically change the pore structure or the chromium oxidation state and the distribution of pillars, but strongly influenced its aggregate morphology. Sulfide-pillared material has an interlamellar distance of 1.01 nm, a BET surface area of 256 m^2 g^{-1}, a micropore volume of 0.082 cm^3 g^{-1} and a pore slit width of 1.24 nm. The chromium sulfide phase in the finely dispersed and well-distributed state that is

reached in sulfide-pillared clay is of primary importance to the high thiophene conversion over this catalyst, also, results exclusively in the formation of butane and butene[76]. However, Li-montmorillonite varying in cation exchange capacity pillared with Cr-pillar precursor ions can provide a family of catalysts that differ in surface area, porous structure and concentration of active sites [86]. The chromium sufide pillared clays exhibit a relatively high stability in thiophene HDS compared to zeolite catalysts which is most likely due to their low protonic acidity.

As for other clays, catalytic activity of Zr-pillaring smectites has been investigated in view of their applications and possible ways to increase their performances. These Zr-pillared clays modified with sulphate ions to produce sulphatedZr-pillars have been claimed, for example, to be active catalysts in cracking and hydrocracking of hydrocarbons, (de)alkylation of (alkyl)aromatics [87] and isomerization of medium alkanes [88]. Occelli and Rennard applied pillared bentonite as a support for Ni-Mo catalysts for the hydrogenation-hydrocracking of vacuum gas oil feedstocks [89]. In both cases the catalysts demonstrated interesting catalytic properties. Radwan et al. [82]investigated the effect of sulfate precursors on the textural properties of the prepared sulfated zirconia pillared bentonite clay catalysts. The intercalated clay was characterized by DTA, FTIR, X-ray diffraction and N_2-adsorption techniques. It was found that, pillaring process using sulfated zirconia as intercalating agent gave rise to good thermal stability, modified structural and textural properties. Catalytic conversion of n-hexane over the prepared catalysts was performed in a flow system operated under atmospheric pressure, at the temperature range 180-300°C. Results indicated that, sulfated zirconia pillared clay (SZ-PILC) catalyst is inferior performance in n-hexane transformation via isomerization, disproportionation and cracking reactions. The higher isomerization activity and selectivity of the modified SZ-PILC at lower temperatures, may inferred to acidity enhancement by the effect of sulfate groups. SZ-PILC catalyst is also active for the formation of di-branched product under the present experimental conditions, which implies that they can meet the demanding criteria for production of higher octane number alkanes.

4.5 Matrix Clays

The ever increasing demand for lighter fuel and higher price of light crude oil have stimulated the petroleum refining industry into looking for the possibility of processing heavy residues as well as the comparatively cheaper heavy crude oils. The major treatment process of the heavy oils is FCC to producehigh octane gasoline with lower sulfur content [38]. However, the main problem associated with the processing of residue/heavy oil is their high organic sulfur and nitrogen content and the presence of other undesirable compounds, which must be removed before further processing due to their toxicity and environmental impact[48]. In general, a desulfurization unit is put after the FCC unit, in order to decrease the

sulfur content, because sulfur regulation in light fuel such as gasoline is very severe: less than 10 ppm[90]. Zeolite is a very active catalyst of FCC [23,26], the pore size of zeolite is relatively small. The large residue/heavy oil hydrocarbon molecules would be unable to diffuse rapidly into the zeolite channels. Moreover, the catalyst particle requires a defined size to able satisfactorily fluidization characteristics in the riser and regenerator. Therefore, to meet the growing demand for lighter and cleaner fuel the need for more efficient catalysts becomes more evident. Further, the key objective in developing a successful catalyst is to achieve maximum catalytic activity under milder reaction conditions.

Modern catalysts of FCC consist, in general, of two major components: zeolite and matrix. An effective matrix must have a porous structure to allow diffusion of hydrocarbons into and out of the catalyst. The activity and selectivity of FCC catalysts are mainly controlled via three processing strategies: zeolite characteristics such as silica/alumina ratio, the presence of additives and the type of matrix in the FCC catalysts as the active matrix can contribute to the cracking reactions[26]. Zeolite is the rate-controlling constituent during the process of catalyst cracking and the matrix performs both physical and catalytic functions [38].

The matrix comprises 60-85 wt% of the commercial FCC catalyst and usually contains synthetic and natural components. The natural component is clay, such as kaolin, bentonite, etc. [91]and amorphous silica or silica-alumina is the synthetic portion[26,38].Thermally and/or chemically modified clays are also used. In these circumstances, new catalytic cracking catalysts, which compose of (a) stabilized zeolite Y, (15-40%)[26] (b) kaolin clays (60-70%) and (c) a binder,have been developed for conversion of heavy oils [13].

As a main matrix, kaolin clays modified the properties of catalytic cracking catalysts, such as reducing coke yield, improving attrition resistance, high tolerance to contaminated metal and high thermal stability. In addition, the matrix zeolite bond stabilizes the zeolite and makes it extremely resistant to sintering or pore collapse and outstanding hydrothermal stability [91].The detailed properties of the matrix can have a profound impact on the properties and performance of a cracking catalyst[38]. Some catalysts also contain one or several additives, designed to boost gasoline octane, increase catalysts metal resistance, reduce SOx emissions, or facilitate CO oxidation. The additive can be incorporated into the catalyst particle or be used as a distinct physical particle. For example, the adding of alumina as additive to the FCC catalyst containing kaolin and silica sol matrix substantially increased the catalyst surface area, acidity and the hydrotreated VGO conversion[26].

Many researchers have focused on the investigation of catalytic cracking catalysts. Hosseinpour et al. [52] and Q. Tan et al. [53] have reported the matrix effect of catalytic cracking. However, these reports are not

enough to understand the role of the matrix in catalytic cracking. The first generation zeolite catalysts were based predominately on $SiO_2.Al_2O_3$ gels ("matrix") in which the zeolite is added at some point prior to spray drying. In the "In-situ" crystallization method as applied by Engelhard, kaolin based microspheres are prepared and calcined, where after zeolites are crystallized in the microsphere, leaving zeolite in an "Al_2O_3-enriched matrix". Gonçalves et al. [38]evaluate the effect of the FCC catalyst components: Y-zeolite, kaolin and aluminaon the formation of coke during the cracking of heavy residue (HR) of petroleum. The catalysts were mixed with a HR at a ratio of approximately 1:4 by using dynamic thermogravimetry (TG) in a furnace at 550°C for 2 h. Y-zeolite, kaolin and Al_2O_3 were analyzed by TG in the same conditions of HR sample. The HR analyzed in these conditions formed 8.1% of coke. All the mixtures presented larger coke formation than that observed in pure HR. The Y-zeolite presented fourfold larger coke formation, while kaolin and alumina showed twofold higher formation than pure HR. It was verified that TG technique has the sensitivity in providing information about coke formation in the catalyst used in fluid catalytic process of refineries.

During the cracking process, heavy metals such as vanadium and nickel are deposited on the catalyst and affect both catalytic activity and selectivity. The study of the interactions between these metals and the components of the matrix of FCC catalysts has remained an important research topic to refiners and catalyst manufacturers. The interaction of vanadium-kaolin was conventionally considered as a physical process in which vanadium species were buried partially in kaolin through adsorption and were therefore passivated. In fact, vanadium species have mobility in the presence of steam at 700-800°C and can migrate onto the surface of zeolite to destroy its framework [75]. So such anti-metal contamination performance of FCC catalyst containing kaolin matrix could not be explained through the physical process; it is therefore important to gain a deeper insight into the interaction of Ni and V-kaolin. Liu et al., [75] compared the hydro-kaolin, acid-modified kaolin (AMK) and caustic-modified kaolin (CMK) containing FCC matrix reacted with vanadium and nickel to form much more mullite. An obvious chemical reaction between Ni and V and kaolin matrix took place at about 700°C. CMK could even be reacted with nickel to form a rather stable $NiAl_{10}O_{16}$ compound and this compound protected zeolite in FCC catalyst effectively. In the presence of suitable vanadium, the temperature of mullite formation during kaolin phase transformation was at least 400°C lower than the conventional mullite formation temperature. Vandium partially replaced Si and Al in the framework of mullite and was therefore passivated, which led to expansion of mullite's unit cell size. Vanadium-mullite forming through kaolin phase transformation in the presence of vanadium at 660-700°C resulted in good anti-metal performance of the FCC catalyst containing modified kaolin matrix (AMK,CMK). In addition, Zheng et al. [92] studied the properties of kaolin and FCC resid

additive prepared from it. The catalysts were characterized by N_2 adsorption, X-ray diffraction, IR characterization and scanning electron micrography (SEM). The results showed that the content of NaY-zeolite synthesized from this kaolin was approximately 25%. The resid additive prepared from above NaY-zeolite exhibited excellent performance for nickel and vanadium passivation, the better gasoline selectivity and coke selectivity, while maintaining high bottoms upgrading selectivity.

Through the FCC process, a significant portion of the feedstock is converted into coke and deposits on the catalyst surface and deactivates the active sites of the catalyst by pore blockage, resulting in important activity loss. In order to recover the activity, coke deposited on catalysts is burnt off in the regenerator, providing heat for the whole system. However, coking will reduce the activity of catalysts and result in the variation of product distribution. This phenomenon is of very significant economic importance and has therefore been the subject of a number of studies. An improvement in the stability of dealuminated mordenite zeolite against coking was observed due to trapping of coke precursors by the kaolin matrix [93].

On the other hand, many researchers investigated the matrix in other processes. Choudhary et al. [94] reported the influence of the addition of alumina or kaolin, as a matrix, to H-Gallosilicate zeolite in propane aromatization. The catalyst deactivation and coke deposition on the zeolite were increased due to the alumina matrix, but when kaolin matrix was used, the coke deposition was not changed significantly. However, the acidity and initial activity/selectivity and time-on-stream activity/selectivity in propane aromatization of gallium-impregnated H-ZSM-5 zeolite catalyst containing 50% matrix, vary according to the type of matrix in the following order: alumina << kaolin < silica [93]. Also, the role of sodium montmorillonite on bounded zeolite catalysts was studied by Cãnizares et al. [95]. The matrix gave the required resistance to the final catalyst, but influenced strong sites density due to partial solid state ion-exchange.

Dorado et al. [96] reported the influence of the agglomeration with a clay matrix on the activity of ZSM-5 and beta zeolite for the hydroisomerization of n-butane. A lower n-butane conversion was always obtained for the bounded catalysts, due to neutralization of some zeolite acid sites. Also, the influence of the bentonite matrix on the catalytic performance of the hydroisomerization of n-octane, using three zeolite-based catalysts: mordenite, beta and ZSM-5 was investigated [97,98]. The n-octane conversion decreased when zeolites mordenite and ZSM-5 were agglomerated with bentonite as compared with that of non-agglomerated ones. However, the catalytic performance of catalysts based on zeolite beta was improved because the presence of extraframework aluminium species provided by the matrix.Whereas, the influence of the impregnation of the catalysts with an

aqueous H_2PtCl_6 solution of about 1 wt% was studied [91].Metal dispersion values were in agreement with the specific surface area of the zeolite in the agglomerated catalysts, suggesting that the metal were mainly located into the zeolite. The presence of the matrix increased the *n*-octane hydroisomerization conversion. Non-agglomerated catalysts, even showing a higher strong acid site density per gram of zeolite, exhibited the lowest *n*-octane conversion. The extraframework aluminium species were present on the agglomerated catalysts enhancing their acid strength through a synergetic effect that allowed them to be much more active for the hydroisomerization of *n*-octane. The influence of the matrix concentration on the isomers selectivity was not significant. According to other studies [94,99], the decrease in the number of strong acid sites can be attributed to solid-state ion exchange between protons of the zeolite and sodium of the clay during the calcination following the ion-exchange step. It has also been reported [97,98] that the agglomeration process can cause a migration of extraframework aluminium species (EFAL) from the clay to the zeolite. This fact has been supported by different authors [91].

4.6 Synthetic Catalysts from Clays

4.6.1 Synthetic Zeolite

Zeolite is widely used as a catalyst in the petroleum and petrochemical industries because of its high concentration of active acid sites, its high thermal stability and high size selectivity. For example, ZSM-5 is widely used as a catalyst for isomerization, alkylation and aromatization processes[21,24]. However, zeolite Y is the most important component in FCC catalysts[23,26]. Today, synthetic zeolites are used commercially more often than natural zeolites due to the purity of crystalline products and the uniformity of particle sizes[38]. Zeolites are usually synthesized from low cost silica-alumina sources in alkaline phase under hydrothermal conditions such as clays[21,22]. The synthetic of zeolite from clay material is analogous to natural formation of zeolite from volcanic deposits or other high Si-Al materials [100,101]. This is because both volcanic ash and natural clay are fine-grained and contain a large amount of alunimosilicate glass. The formation of natural zeolite may take thousands of years; however, laboratory preparation can shorten this period to hours[21].

Kaolin is the most versatile industry mineral and is extensively used for synthetic zeolite[21-24]. The benefits of using kaolin as an aluminosilicate source in zeolite synthesis widely known [21,22,38,100,101].The analysis of the natural kaolin clay shows that the clay contains very low concentration of leachable metals (Pb, As, Zn) which negatively affects catalyst performance, thereby making the kaolin clay an excellent raw material for the production of zeolite for catalysis[21].Many variable parameters are strongly influenced on the formation of zeolite from kaolin. The important parameters are starting material composition, amount of added water, ageing temperature, ageing time,

crystallization temperature and crystallization time[23]. Zeolites prepared from kaolin are always contaminated with trace amount of iron, titanium, calcium, magnesium, etc. which are originally present in the natural kaolin. These elements may have some influence on the zeolite properties such as brightness, hardness, catalytic activity, electrical properties, etc. Various zeolites from kaolin have been synthesissuch as 4A, ZSM-5, mordenite, X-, Y-zeolites, etc. Kaolin is usually used after calcination to obtain a more reactive phase metakaolin, with the loss of structural water. Only a small part of AlO_6 octahedra is maintained, while the rest are transformed into much more reactive tetra- and penta-coordinated units. The conditions of the kaolin calcination strongly influence the reactivity of the obtained solids. The best conditions for obtaining a very reactive metakaolin have been discussed by several authors who reported values between 600-800°C. Other types of clays, such as, illite, smectite, interstratified illite-smectite, montmorillonite and bentonite are used for synthesis of zeolites.

Presently, many researchers are working actively in various aspects on the synthesis of zeolite from kaolin.A hydrothermal synthesis method for ZSM-5 preparation was investigated by using expanded perlite and kaolin as the only alumina source. The ZSM-5 zeolites from the expanded perlite and kaolin have distinctive pore systems which were a combination of a medium pore ZSM-5 zeolite and a large pore matrix perlite (or kaolin). The dual-function of ZSM-5 zeolites with zinc from the expanded perlite (or kaolin) showed a better catalytic activity in the FCC naphtha aromatization reaction compared with ZSM-5 obtained by an ordinary method[24].Anotherinvestigation, the effect of different concentration of NaOH for the hydrothermal synthesis of ZSM-5 zeolite from local kaolin clay material was studied by Oghenejoboh and Ohimor[21]. It was concluded that at high concentration of NaOH, all the physical properties of the produced zeolite exhibit that the clay can be used to synthesis zeolite of high quality that may be used as catalysts in oil refineries, drying and purification agents in natural gas processing as well as in sludge and wastewater treatment. It is also shown that 5.5 M NaOHsolution can be used to synthesis low moisture content ZSM-5 zeolite which is used in the FCC unit.

Htay and Oo synthesized zeolite Y with SiO_2/Al_2O_3 molar ratio of 3.53 from kaolin under hydrothermal condition [23]. The samples were characterized by X-ray Diffraction, Scanning Electron Microscope and analyzed by gravimetric method. The results show that the typical zeolite Y can be prepared with a molar composition of $6SiO_2:Al_2O_3:9Na_2O:249H_2O$. The catalytic activities of prepared zeolite NaY, NH_4Y and HY were investigated by using the laboratory scale fixed-bed catalytic cracking unit. The cracking process of heavy gas oil was carried out with catalyst to oil ratio of 3 at the reaction temperature of 450-510°C. The results of cracking selectivity by NaY, NH_4Y and HY are shown in Table 3. Among the three catalysts, the modified zeolite HY

exhibited the highest activity for cracking the feed to gasoline. It was reported that the synthesized zeolite from kaolin had an ion exchange capacity of 4.72-4.94 meq/g with a stable structure between 400°C and 600°C but collapsed above 600°C. For the purpose of catalytic process (as catalytic cracking), operating condition seldom exceed 600°C, structural stability regime of the samples[102]. Also, the synthesis of NaY zeolite with coal-based kaolin was studied by Liu and Yan [103].

Table 3: The evaluating results of lab-scale fixed-bed caracking column

Catalyst	NaY	NH₄Y	HY
Product yield, vol%	19.7	18.3	14.0
Gases	26.0	31.0	43.0
Gasoline	10.7	15.8	12.7
Kerosene	12.5	5.9	5.2
Diesel oils	7.6	5.9	4.5
Heavy oils	7.5	6.4	2.6
Coke	74.0	83.3	82.0

4.6.2 Synthetic alumina

As mentioned above, the low cost of kaolin has been identified as a potential raw material for the production of zeolite and in addition for the production of alumina (γ-Al$_2$O$_3$). Alumina is one of the most widely used as a catalyst and catalyst support material in many industries such as hydrotreating processes[6,29]. Several authors have described the direct conversion of kaolin into γ-Al$_2$O$_3$ by thermal treatment followed with acid or base extraction. Okadaet al. [104] and Samadhi et al. [6] described the synthesis of γ-Al$_2$O$_3$ from calcined kaolin via the selective extraction of the amorphous SiO$_2$ phase by concentrated potassium hydroxide (KOH) solution. The highest specific surface area of 233 m^2/g was obtained when the kaolin was calcined at 1000°C for 24 h and the metakaolin was extracted for 12 h. The solid residue remaining after the extraction was identified as having a spinel structure, containing γ-Al$_2$O$_3$ and a minor content of crystalline SiO$_2$. Saito et al. [105] studied the effect of kaolin calcination temperature on the pore structure of γ-Al$_2$O$_3$ produced via extraction by KOH solution. At calcination temperatures in the 950-1050°C range, these authors obtained a specific surface area of 250 m^2/g.

Extraction by acidic solution represents another route for the synthesis of γ-Al$_2$O$_3$ from kaolin. Contrary to the basic solution extraction route, the acidic solution extracts the alumina phase from the kaolin crystal structure. This implies that the acid extraction route necessarily involves additional steps to recover the alumina from the extract and to convert the recovered solid material to γ-Al$_2$O$_3$ by calcination. Belver et al. [30] described the reaction between a Spanish kaolin calcined between 600-900°C and concentrated HCl solution. This reaction removes most of the octahedral Al^{3+} from the kaolin crystal structure, leaving behind a network structure consisting of amorphous silica phase. Yang et

al.[31] also described a synthesis route of γ-Al$_2$O$_3$ from kaolin by acid extraction. The suspension extract produced by contacting kaolin and concentrated HCl solution was filtered and precipitated by adding ammonia.

The obtained precipitate contained boehmite and aluminum hydroxide, which started to form γ-Al$_2$O$_3$ at 537°C during calcination. Hosseini et al.[29] reported that kaolin could be promising material for preparation of γ-Al$_2$O$_3$ by calcination at 800°C and extracted via H$_2$SO$_4$ and consequently precipitation in ethanol. The precipitated was dried and calcined at 900°C, which resulted the formation of γ-alumina. In agreement with other works, it is resulted that the main factor in obtaining of different alumina phases is the calcination temperature. Calcination at 680-1030°C leads to form the γ-Al$_2$O$_3$[32]. In addition, it was concluded that the largest surface area values of 365 and 405 m^2/g were obtained for the 700°C and 800°C calcined bentonite clay and dry acidified samples respectively and this results is satisfied for the surface area requirement for catalyst support when compared to the literature values 150 to 350 m^2/g for commercial montmorillonite clay supports for FCC catalyst[28].

5.   OTHER APPLICATIONS

At the petrochemical enterprises, aromatic streams obtained from catalytic reforming and cracking processes always contain undesirable trace olefins [106] which are harmful to the downstream technological processes and the applications of aromatics [107]. Hence, the impurities must be removed before aromatic streams are routed to the petrochemical processes provided with the suitable treatment technologies [108]. Two processes have been proposed for removing trace olefins from aromatics (i.e., activated clay treating and catalytic hydrogenation treating) and currently most refineries in China are still using the clay treatment technologies to remove olefins [108]. However, the commercial clay material has a very limited lifetime and should usually be land-filled when it is discarded, which will definitely cause pollution to the environment.

In order to achieve better performance of the scale-up product, different additives that would be modifying the synthesized catalyst were investigated [108], which can alleviate the catalyst deactivation effectively.The catalysts were the clay modified via incorporating the transition metal ions without additive and through kneading catalyst with different additives such as metal halide additive; zeolite; and activated carbon. The catalytic activity tests of three aromatics samples were carried out in a fixed-bed tubular micro-reactor, at a reaction temperature of 175°C and a WHSV of 30 h^{-1}. The inlet and effluent liquids to and from the reactor were analyzed by a bromine index analyzer. The lifetime of the catalyst was increased from 5 h to 8 h upon specifying the conversion of the olefins equating to more than 55% as a criterion. It should be noted that the metal halide additive catalyst maintained a higher activity than other catalysts for removing trace olefins from the aromatics stream and increased the amount of the weak

Lewis acids (Fig. 6). The X-ray diffraction patterns had verified that the additive was highly dispersed on the surface of catalyst.

6. CONCLUSIONS

Petroleum refining industry has been continuous developed, which include processes that are based on the catalysts.Catalysts by clays have attracted much interest recently and an important catalytic application in petroleum refining industry. Clays and their modifications are used extensively for various processes such as catalytic cracking, hydrocracking, isomerization, alkylation, etc. Pillared clays are very interesting and promising catalysts in a broad range of application. Kaolin is versatile industry clay and is extensively used in the manufacture of catalysts. The largest use of kaolin is in the catalytic cracking of petroleum.In addition, kaolin is extensively used for the synthetic of zeolite and alumina and in the matrix as catalysts of FCC. However, the clay most widely used as an efficient solid acid-catalyst is montmorillonite. Further, palygorskite and sepiolite clays are being used increasingly as catalyst supports.
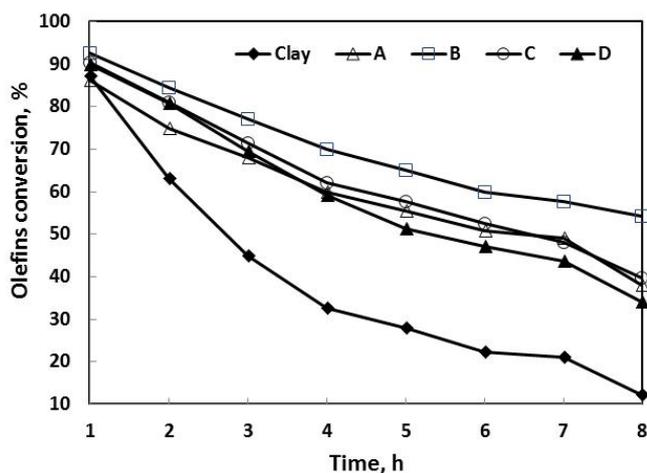
Fig 6: The influence of different additive, A: no additive; B: metal halide additive; C: zeolite additive and D: activated carbon additive.

REFERENCES

[1]   Speight J G. Handbook of petroleum products analysis. John Wiley & Sons, Inc., Hoboken, New Jersey. ISBN: 0-471-20346-7. 2002

[2]   Speight J G. The chemistry and technology of petroleum.4th Edition, CRC press, Wyoming US. ISBN- 10: 0-8493-9067-2. 2006

[3]   Kaur N, Kishore D. J Chem Pharm Res, 2012, 4(2):991

[4]   Mohan S R, Sàmano V, Ancheyta J, Diaz J A I. Fuel, 2007, 86: 1216

[5]   Silvy R P. ApplCatal A, 2004, 261:247

[6]   Samadhi T W, Subagjo, Lismana K R, Fuadi K. ITB J EngSci, 2011, 43(2): 113

[7]   Bartholomew C H. Catalytic hydroprocessing of petroleum and distillates. In: Oballa M C, Shih S S, editors. New York: Marcel Dekker, 1994

[8]   Choudhury T, Misra M N. Bull Mater Sci, 2011, 34(6): 1273

[9]   Centi G, Perathoner S. Microporous and Mesoporous Materials, 2008, 107: 3

[10]   Murray H H. Applied clay mineralogy. 1st edition, Copyright © 2007, Elsevier B.V., ISBN-13: 978-0-444-51701-2

[11]   Venkatathri N. Bull CatalSoc India, 2006, 5: 61

[12]   Rodrigues M G F. Cerâmica, 2003, 49: 146

[13]   Rong T-J, Xiao J-k. Mater Lett, 2002, 57: 297

[14]   Campanati M, Vaccari A. Fine chemicals through heterogeneous catalysis. In: Sheldon R A, Bekkum H V, Herman H (Eds). Wiley–VCH, Weinheim, Germany, 2001, 61

[15]   Choudary B M, Chowdari N S, Kantam M L. Tetrahedron, 2000, 56: 7291

[16]   Jankovič Ĺ, Dimos K, Bujdák J, Koutselas I, Madejová J, Gournis D, Karakassidesb M A, Komadel P. Physical Chemistry Chemical Physics, 2010, 12: 14236

[17]   Herrero J, Blanco C, Esteruelas M A, Oro L A. ApplOrganometalChem, 1990, 4: 157

[18]   Mishra T. Pillared clays and related catalysts. A. Gil et al. (eds.). Springer, New York, 2010, 99

[19]   Turgutbasoglu F, Balci S. Proceedings of the 13th International Clay Conference, Waseda University, Tokyo, Japan, 2005

[20]   Hettinger W P Jr. Appl Clay Sci, 1991, 5: 445

[21]   Oghenejoboh K M, Ohimor E O. European J Sci Res, 2011, 56(4): 445

[22]   Ajayi A O, Atta A Y, Aderemi B O, Adefila S S. J ApplSci Res, 2010, 6(10): 1539

[23]   Htay M M, Oo M M. World Academy of Science, Engineering and Technology, 2008, 48: 114

[24]   Wang P, Shen B, Shen D, Peng T, Gao J. Catalysis Communications, 2007, 8: 1452

[25]   Venkatathri N. Mater Sci Res India, 2005, 3: 111

[26]   Al-Khattaf S. Energy & Fuels, 2003, 17: 62

[27]   Murray H H. Clay Minerals, 1999, 34: 39

[28]   Salahudeen N, Ahmed A S, Ajinomoh C S, Hamza H. Petroleum Technology Development Journal, 2012, 2(2): 1

[29]   Hosseini S A, Niaei A, Salari D. Open Journal of Physical Chemistry, 2011, 1: 23

[30]   Belver C, Munoz M A B, Vicente M A. Chem Mater, 2002, 14: 2033

[31]   Yang H, Liu M, Jing O. Appl Clay Sci, 2010, 47: 438

[32]   Wang S, Li X, Wang S, Li Y, Zhai Y. Mater Lett, 2009, 62(20): 3552

[33]   Curini M, Rosati O, Costantino U. Curr Org Chem, 2004, 8: 591

[34]   Ding Z, Kloprogge J T, Frost R L, Lu G Q, Zhu H Y. J. Porous Mater, 2001, 8: 273

[35]   Naman S A, Maher K A, Ibrahim R P. Journal of Petroleum and Gas Exploration Research,2012, 2(4): 80

[36]   Hsu C S and Robinson P R (eds). Practical advances in petroleum processing. New York City: Springer, 2006

[37]   Harding R H, Peters A W, Nee J R D. ApplCatal A, 2001, 221: 389

[38]   Gonçalves M L A, Barreto J R C, Cerqueira W V, Teixeira A M R F. J Therm Anal Calorim, 2009, 97:515

[39]   SunS-H，MaJ-T，PangX-M，SunY-B，Wang S-L. Bull CatalSoc of India, 2005, 4: 72

[40]   Moronta A, Ferrer V, Quero J, Arteaga G, Choren E. ApplCatal A, 2002, 230: 127

[41]   Lee K-Y, Ko K-Y. Bull Korean ChemSoc, 2004, 25: 1929

[42]   Keith M. Handbook of green chemistry and technology. In: Clark J, Macquarrie D (Eds.). Blackwell Science Ltd., Oxford, UK, 2002, 321

[43]   de Paiva L B, Morales A R, Dìaz F R V. Appl Clay Sci, 2008, 42: 8

[44]   Melo D M A, Ruiz J A C, Melo M A F , Sobrinho E V, Martinelli A E. Journal of Alloys and Compounds, 2002, 344: 352

[45]   Edah A O, Kolawole J A, Solomon A O, Shamle N, Awode A U. J Res Environ Sci Toxic, 2012, 1(2): 19

[46]   Barbel S, Kurnianwan T A. J Hazardous Mater, 2003, B97: 219

[47]   Costanzo P M. J. Clays and Clay Minerals, 2001, 49(5): 372

[48]   Hossain M M, Al-Saleh M A, Shalabi M A, Kimura T, Inui T. ApplCatal A, 2004, 274: 43

[49]   Hossain M M, Al-Saleh M A, Shalabi M A, Kimura T, Inui T. ApplCatal A, 2004, 278: 65

[50]   Aoki K, Minato Y, Torii K, Shirai M, Arai M. ApplCatal A, 2001, 215: 47

[51]   Arai M, Minato Y, Torii K, Shiraj M. CatalLett, 1999, 61: 83

[52]   Hosseinpour N, Mortazavi Y, Bazyari A, Khodadadi A A. Fuel Process Technol, 2009, 90: 171

[53]   Tan Q, Bao X, Song T, Fan Y, Shi G, Shen B, Liu C, Gao X. J Catal, 2007, 251: 69

[54]   Yadav G D, Doshi N S. ApplCatal A, 2002, 236: 129

[55]   Nagendrappa G. Resonance, 2002, 7(1): 64

[56]   Galan E. Clay Minerals, 1996, 31: 443

[57]   Vogels R J M J, Kloprogge J T, Geus J W. J Catal, 2005, 231(2): 443

[58]   DeStefanis A, Tomlinson A A G. Catal Today, 2006, 114: 126

[59]   Williams G R, O'Hare D. J Mater Chem, 2006, 16: 3065

[60]   Guggenheim S, van Groos A F K. Clays and Clay Minerals, 2001, 49: 433

[61]   Zheng S, Sun S, Zhang Z, Gao X, Xu X. Bull CatalSoc India, 2005, 4: 12

[62]   Kellendonk F J A, Heinerman J J L, van Santen R A. Clay-activated Isomerization Reactions. Academic Press.Inc., 1987. 455

[63] Plee D, Schutz A, Poncelet G, Fripiat J J. In catalysis by acids and bases. B. Emelik et al., eds., Elsevier, Amsterdam, 1985. 343

[64] Yadav M K, Chudasama C D, Jasra R V. J MolCatal A: Chem, 2004, 216: 51

[65] Linbo C, Li S. China Pet Process Petrochem Tech, 2011, 13(1): 38

[66] Hart M P, Brown D R. J MolCatal A: Chem, 2004, 212: 315

[67] Jasra R V. Bull CatalSoc India, 2003, 2: 157

[68] Elangovan S P, Cischof C, Hartmann M. CatalLett, 2002, 80: 35

[69] Ali M A, Kimura T, Suzuki Y, Al-Saleh M A, Hamaid H, Inui T. ApplCatal A, 2002, 227: 63

[70] Hossain M M. ChemEng J, 2006, 123: 15

[71] Kimura T, Al-Nawad K, Ali S A, Suzuki Y, Hamid H, Inui T. in: Proceedings of the 220th ACS National Meeting, Washington, August 20-24, 2000

[72] Al-Saleh M A, Hossain M M, Shalabi M, Kimura T, Inui T. ApplCatal A, 2003, 253: 453

[73] Riad M, Saad L, Mikhail S. Australian J Basic and ApplSci, 2008, 2(2): 262

[74] Melo D M A, Ruiz J A C, Melo M A F, Sobrinho E V, Schmall M. Microporous and Mesoporous Materials, 2000, 38: 345

[75] Liu C, Deng Y, Pan Y, Zheng S, Gao X. ApplCatal A, 2004, 257: 145

[76] Sychev M,(San) de Beer V H J, Kodentsov A, van Oers E M, van Santeny R A. J Catal, 1997, 168: 245

[77] Feng L, Duan X. Layered Double Hydroxides Struc Bond, 2006, 119: 193

[78] Gyftopoulou M E, Milian M, Bridgwater A V, Dugwell D, Kandiyoti R, Hriljac J A. ApplCatal A, 2005, 282: 205

[79] Belkhadem F, Clacens J-M, Bengueddach A, Figueras F. ApplCatal A, 2008, 298: 188

[80] Issaadi R, Garin F, Chitour C E, Maire G. ApplCatal A, 2001, 207: 323

[81] Vaughan D E W, Lussier R, in: L.C. Rees (Ed.). Proceedings of the 5th International Conference on Zeolites, Naples 1980, Heyden Press, London, 1980

[82] Radwan D, Saad L, Mikhail S, Selim S A. J ApplSci Res, 2009, 5(12): 2332

[83] Xiaolin T, Zheting L, Li S. China Pet Process Petrochem Tech, 2011, 13(3): 16

[84] Sugioka M, Kanda Y, Kobayashi T, Uemichi Y. MemMuroranInst Tech, 2004, 54: 41

[85] Kloprogge J T, Welters W J J, Booy E, de Beer V H J, van Santen R A, Geus J W, Jansen J B H. ApplCatal A, 1993, 97: 77

[86] Sychev M,de Beer V H J, van Santen R A. Microporous Materials, 1997, 8: 255

[87] Johnson J W, Brody J F, Soled S L, Gates W E, Robbins J L, Maruchi-soos E. J MolCatal, 1996, 107: 67

[88] Jong S J, Lin J T, Chen S, in: Hattori T, Yashima T (Eds.). Studies in Surface Science and Catalysis, Kodansha/Elsevier, Tokyo/Amsterdam, 1994, 83: 33

[89] Occelli M L, Rennard R J. Catal Today, 1988, 2: 309

[90] Ishihara A, Hashimoto T, Nasu H. Catalysts, 2012, 2: 368

[91] Sánchez P, Dorado F, Fúnez A, Jiménez V, Ramos M J, Valverde J L. J MolCatal A: Chem, 2007, 273: 109

[92] Zheng S, Sun S, Wang Z, Gao X, Xu X. Bull CatalSoc India, 2005, 4: 30

[93] Choudhary V, Sivadinarayana C, Mantri K. Proc Indian AcadSci (ChemSci), 1999, 111(5): 669

[94] Choudhary V R, Devadas P, Kinage A K, Guisnet M. ApplCatal A, 1997, 162: 223

[95] Cãnizares P, Duŕan A, Dorado F, Carmona M. Appl Clay Sci, 2000, 16: 273

[96] Dorado F, Romero R, Cãnizares P. ApplCatal A, 2002, 236: 235

[97] de Lucas A, Valverde J L, Sánchez P, Dorado F, Ramos M J. ApplCatal A, 2005, 282: 15

[98] de Lucas A, Valverde J L, Sánchez P, Dorado F, Ramos M J. IndEngChem Res, 2004, 43: 8217

[99] Romero M D, Calles J A, Rodŕguez A, De Lucas A. MicroporousMesoporous Mater., 1997, 9: 221

http://www.ejournalofscience.org

[100] Koukouzas N. Ptolemais, Northern Greece, Internal Journal of Coal Geology, 2007, 71(2-3): 276

[101] Moutsatsou A, Stamatakis E, Hatzitzotzia K, Protonotario V. Fuel, 2006, 85 (5-6): 657

[102] Atta A Y, Ajayi O A, Adefila S S. J ApplSci Res, 2007, 3(10): 1017

[103] Liu X, Yang Z. J Natural Gas Chemistry, 2003, 12: 63

[104] Okada K, Kawashima H, Saito Y, Hayashi S, Yasumori A. J Mater Chem, 1995, 5(8): 1244

[105] Saito Y, Hayashi S, Yasumori A, Okada K. J Porous Mater, 1996, 3: 233

[106] Brown S H, Waldecker J R, Lourvanij M. US 7744750[P], 2005

[107] Chen C W, Wu W J, Zeng X S. IndEngChem Res, 2009, 48(23): 10359

[108] Xin P, Li S. China Pet Process and Petrochem Tech, 2012, 14(2): 44