

# Modification and Evaluation of the Potential of Nigerian Bentonite Clays as Catalysts Support for Upgrading Heavy Crude Oil and Bitumen

*Philip Shallsuku*

## ABSTRACT

*In this work, bentonite clays obtained from north-eastern Nigeria were acid-activated, which induced structural changes with the formation of pore sizes classified according to the International Union for Pure and Applied Chemistry (IUPAC) as macropores (50nm), Mesopores (2 to 50nm), and micropores (up to 2nm). 3wt.% metal oxide nanoparticles were supported on the mesoporous-macroporous bentonite, which contains 80-97% montmorillonite by a modified incipient wetness impregnation method. The catalytic performance was assessed in cracking of asphaltenes in heavy crude oil and petroleum residue. Based on the result, it is reported that the metal oxide nanoparticles catalysts were able to substantially reduce the formation of coke and showed a better asphaltene conversion. Obviously, due to the nature of the chemical bonding between the support and the metal atoms, the electronic properties-and the reactivity-of the metal is affected. For instance, acidity in the support is known to facilitate the decomposition of asphaltenes but it will also promote cracking. In general, a strong interaction between metal and support makes a catalyst more resistant to sintering and coking, thus resulting in a longer time of catalyst stability. Catalysts were characterized by chemical composition through X-ray Fluorescence, surface area, and pore size distribution through N<sub>2</sub> adsorption/desorption, catalyst acidity by temperature programmed desorption (TPD), and metal dispersion by pulse H<sub>2</sub> chemisorption. Batch adsorption experiments and catalytic cracking of adsorbed heavy fractions were carried out with heavy oil containing asphaltenes, resins and bitumen. The bentonite clay studied here is a promising alternative support material for catalyst preparation because, as a natural resource, it does not require synthesis processes, which can be quite expensive. This work creates new possibilities for the use of bentonite functionalized with metal oxide nanoparticles as catalysts for upgrading heavy crude oils and bitumen. The study also provides an insight into potential applications of nanoparticles technology for heavy oil processing and production, which could be a viable alternative green technology.*

**Keywords:** *Bentonite clay, catalysts support, heavy crude oil, bitumen, upgrading, Asphaltene.*

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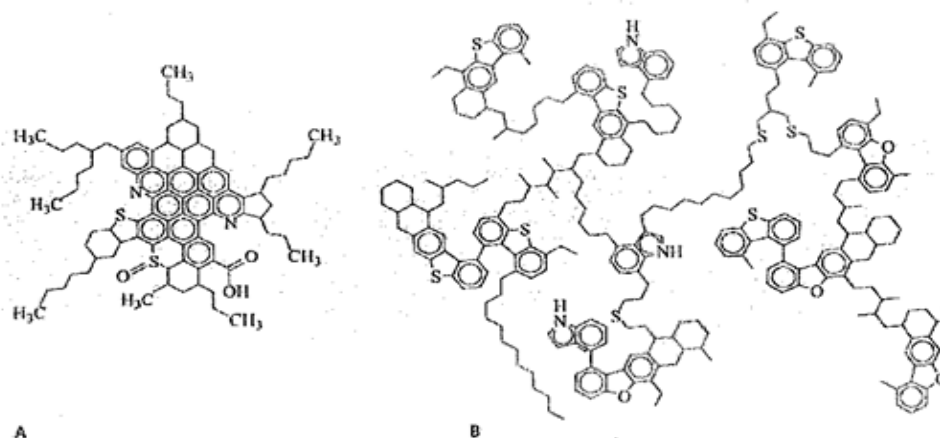
## INTRODUCTION

In the petroleum refinery, recent efforts have been focused on the development of effective and efficient conversion and upgrading of crude oils into valuable light fuels. With the increase in consumption of fossil fuels, research on conversion and upgrading of unconventional resources such as heavy and extra heavy crude oils have become one of the major concerns in the past several years. In unconventional crude oils, there are large amount of atmospheric residue (AR) and vacuum-distilled residue (VR) that could be obtained and transformed into other valuable chemical feedstock and lighter fuels such as gasoline (Ancheyta, Centeno, Trejo, and Marroquin, 2003).

These residues are the heaviest fractions obtained from the fractional distillation processes, which mainly consist of larger amount of hydrocarbon molecules such as asphaltenes, heteroatoms compounds such as Sulfur, nitrogen and oxygen compounds, and heavy metals (Hart, Leeke, Greaves and Wood, 2014). Traditionally, these oil residuals [AR and VR] can be processed via thermal cracking (Rana, Samano, Ancheyta and Diaz, 2007), catalytic cracking (Hassan, Ghannam and Esmail, 2010), and hydrocracking (Shan and Guang, 2001). However, these processes are still limited primarily due to catalysts deactivation and coke formation (Veith, 2007). In addition, large amount of hydrogen is required to reduce the effect of coke formation (Hart, Leeke, Greaves and Wood, 2014). This is still considered ineffective and costly.

Recently, the application of nano-materials in conversion and upgrading process of heavy crude oil and its derivatives have attracted much attention since nanocatalysts provide a large surface area for the appropriate catalytic reactions (Hart, *et al.*, 2014). Over the last few years, different types of nanocatalysts such as metal oxide nanoparticles have been used in hydro-processing of crude oil due to their good asphaltenes adsorption/oxidation and their high oxygen storage/release capacity (Hart, *et al.*, 2014). As with the other classes of compounds, the asphaltenes component of heavy crudes and bitumen is also significantly different from that of light crudes (Hart, *et al.*, 2014). In addition to the high heteroatom and metal content, asphaltenes have significantly higher molecular weights, due to the high concentration of sulphur which favours the formation of sulphide and disulphide bridges among the aromatic clusters, a characteristic which makes these structures very reactive in relation to thermal cracking and hydrogenating reactions (Hart, *et al.*, 2014). From the molecular point of view, the asphaltenes contained in bitumens can be represented effectively by 'archipelago' models, that is, structures made up of islands of little groups of condensed rings, linked together by aliphatic chains and sulphide bridges, as depicted in Fig.1 (Ancheyta, Centeno, Trejo, Marroquin, 2003; Speight, 1998, 2004; Groenzin and Mullins, 1999).





**Figure 1:** Average molecular structures representing asphaltene molecules from different sources: A, asphaltenes from traditional crude; B, Asphaltene from Nigerian Crude Oil (Speight, 2004; Shallsuku, 2008).

The ideal catalyst for the upgrading of heavy feedstocks must facilitate the process of hydrogen addition to the products generated in the thermal cracking phase, minimizing the amount of coke produced (Hart, Shah, Leeke, Greaves and Wood, 2013). Moreover, it must permit the removal of the poisons present in the feedstock through hydrogenation of the substrate, or rather it must favour the processes of desulphurization (HDS, Hydrodesulphurization), denitrogenation (HDN, Hydronitrogenation), demetallization (HDM, Hydrodematallization) and reduction of carbon residue from the products (HDCCR, Hydro Conradson Carbon Residue Removal) (Encyclopaedia of hydrocarbons, p.137, Volume. III).

The most active catalytic species for these reactions are certain heavy metal oxides such as Mo, Ni, Co, W and Rh in particular, often used in combinations (Ni/Mo, Co/Mo and Ni/W) and deposited on appropriate porous supports (preferably alumina) or mixed with the feedstock in the form of powder (catalysis in slurry phase) [Hassan, *et al.*, 2013]. The main problem that is encountered when using supported catalysts to process particularly heavy feedstocks is that of limiting the deactivation of the catalyst due to the depositing of both the metals and coke (Fukuyama, Nakamura and Ikeda, 2010). However, it should be made clear that the deposited coke can be removed through regeneration of the catalyst, whereas the activity loss due to the metals is permanent and, hence, the catalyst has to be replaced (Contreras, and Fuentes, 2013). The deactivation due to deposits of coke leads to a loss of activity because the active sites of the catalyst are covered by carbonaceous materials, primarily from asphaltenes; in fact, this loss increases with the level of conversion of the feedstock into distillates, that is, when conditions favour

the emergence of stability problems [Ghanavati, Ahmad Ramazani and Mohammad-Javad, 2013]. The deactivation by coke can be offset by an increase in the hydrogen partial pressure (Hart, *et al.*, 2013; Maity, Blanco, Ancheyta, Alonso and Fukuyama, 2012]. As regards the metals, the deactivation comes about through the obstruction of the porous structure and the covering of the active sites by the metals contained in the metallo-porphyrinic structures which are destroyed during the reaction generating the corresponding sulphides.

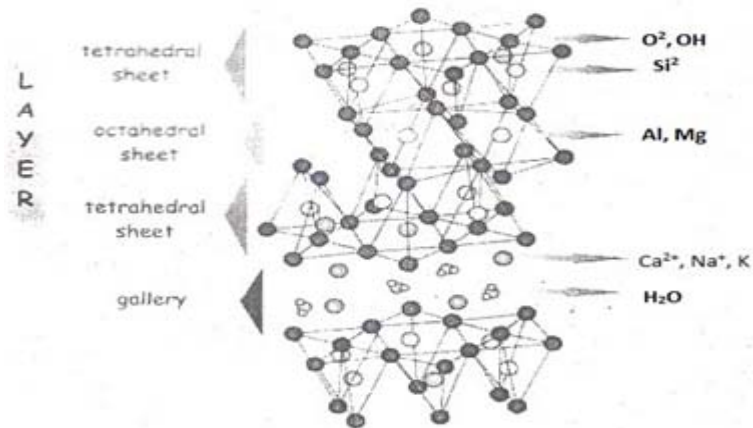
However, the physical characteristics of the support and, in particular, its porosity are as fundamentally important as those of the active phase in determining presence of high molecular weight compounds (asphaltenes and metallo-organic compounds), which are characteristics of heavy feedstocks, make access to the substrate within the catalyst particles difficult; the diffusion process within the porous structure can be a problem and can represent the slow stage of the reaction (Furimsky, 2007). If the catalyst does not have a sufficiently porous structure and the diffusion of the molecules in the pores is impeded, most of the metals are deposited on the external surfaces, causing obstruction of the pores and, therefore, impeding the reaction.

Consequently, in the case of heavy feedstocks, macroporous materials are used, often as 'sacrificial beds', on which most of the demetallization reactions are made to take place in order to go ahead with the conversion reactions and upgrading of the feedstock using *ad hoc* catalytic beds. The use of smectic in catalysis began in the mid-1930s when acidified montmorillonites were used as catalysts in petroleum cracking reactions (Occelli and Rennard, 1988; Pinnavaia, 1983; Thomas and Thomas, 1997). By the 1970s, the possibility of modification of these clay minerals by other processes, including the pillaring or intercalation of anions, complexes and organic compounds between layers of clay minerals, was discovered (Figueras, 1988; Vaughan, 1988). These modifications led to new material properties and reactivities that extended the applications of this group of clay minerals as catalysts (Gonzalez *et al.*, 1999; Sanabria, Alvarez, Molina, Morenzo, 2008; Swarnakar *et al.*, 1996). The most common method of transforming smectic into active materials for adsorption and catalysis involves treating raw bentonite with acidic solutions, leading to the formation of solids with sufficient acidity for use in processes (Laszlo, 1987, 1990; Sabu, Sakumar, Rekha and Lalithambika, 1999).

The main component of bentonite, montmorillonite is the clay mineral composed of the layers containing two sheet built of silicon oxide tetrahedrals and placed between them the sheet of aluminum oxide octahedrals, where one third of oxygen atoms form hydroxyl groups [Zhou and Keeling, 2013].  $Al^{3+}$  ions are partly replaced by the cations with lower valence, which results in the negative charge of the whole layer (Schoonheydt, 2002). This charge is balanced by cations. The most often  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  or  $Mg^{2+}$  situated in interlayer spaces



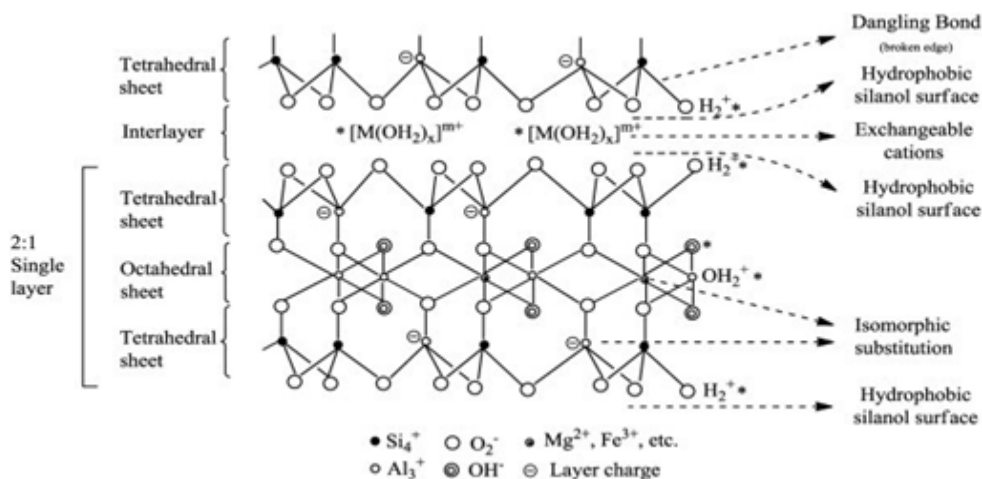
(Schoonheydt, 2002). Extra-framework cations can take part in the ion exchange or a chemical reaction enabling the introduction of organic substances into galleries. The structure of montmorillonite is presented in Figure 2.



**Figure 2.** Montmorillonite structure

**Source:** Tran, Dennis, Milev, Kamali Kannangara, Wilson and Lamb (2005).

In clay minerals, the active sites may arise from 1. “Broken edge” sites and exposed surface of aluminol and silanol groups, 2. Isomorphic substitutions, 3. Exchangeable cations, 4. Hydrophobic silanol surfaces, 5. Hydration shell of exchangeable cations, and 6. Hydrophobic sites adsorbed inorganic molecules (Figure. 3). These peculiar chemical features combined with the nanometer scale layering and the interlayer spacing, allows for a variety of functional materials with potential applications in advanced technologies, in particular, nanotechnology (Zhou & Keeling, 2013).



**Figure 3:** Schematic drawing of 2:1 – type clay mineral showing active sites (Zhou & Keeling, 2013).

Considering the development of clay minerals as catalysts, their chemical functions generally need to be intensified to improved efficiency.

Possible ways of making ‘*catalytically active sites*’ within and onto the matrix of clay minerals are with active species in the framework of clay minerals, which can be made accessible; through the ions within the interlayer space, judiciously exchanged with active components for catalysis purpose; with functional nanoparticles (NPs) or clusters onto or within the clay nanostructure [Zhou & Keeling, 2013].

Even though the preparation and modification of different types of nanomaterials have been widely investigated, the functionalization of nanomaterials aimed at applications in oil and gas industry is still unclear. More studies on the specific functionalization on nano-materials are needed. Many kinds of processes such as thermal cracking, catalytic cracking hydrocracking and thermal catalytic steam gasification are methods proposed for the partial upgrading of the heavy oil and are based on the cracking of compounds with more than 30 molecules of carbon [Nassar, Hassan and Pereira-Alao, 2011].

However, carbon residue deposition, catalyst deactivation due to the heavy metals content in the feedstock (such as Ni, V) are the most common problem related to heavy oil upgrading on surface demands the development of catalyst with the ability to adsorb the heaviest fraction and then promote the cracking of adsorbed molecules with a low coke production (Franco, Lozano, Acevedo, Nassar and Cortes, 2015). The catalyst comprises of an active phase preferably supported on a macro or mesoporous material [Nguyen-Huy and Shin, 2016].

Several researchers have reported the adsorptive behaviour between the heavy oil fraction with carbon, clays, kaolin, silica, and alumina (Lopez-Linares, Nassar, Carbognani-Arambarri and Pereira-Almao., 2013) evaluated the visbroken residue and the asphaltenes adsorption on kaolin and clay, associating the high aromaticity and nitrogen content with the adsorptive behaviour of the heavy fraction. (Carla Schmidt, Min Zhou, Hazel Marriott, Nina Morgner, Argyris Politis and Carol V. Robinson, 2013) suggested the hydrogen production based on the adsorption and gasification of the unstable heavy fraction during the visbreaking process with kaolin as the adsorbate. Due to the low cost of the mesoporous materials, textural properties modification as pore size and surface area are used to improve the adsorptive capacity [Groen, Peffera and Pérez-Ramírez, 2003]. The active phase comprises of metal oxides on the support surface, and there are mostly Ni, Mo, W and Co [Groen, Peffera and Pérez-Ramírez, 2003].

In this context, the primary objective of this work is the evaluation of bentonite clays obtained from north-eastern Nigeria, functionalized with nanoparticles of NiO and PdO in the decomposition of heavy fractions of crude Oil and bitumen such as resins and asphaltenes. The adsorption behaviour of the crude oil heavy compounds was described and correlated with the catalytic



activity of these materials. The effect of NiO and PdO nanoparticles supported on the montmorillonite of bentonite clay in catalytic cracking of asphaltenes was investigated in comparison with the bentonite clay support alone. In Nigeria, bentonite deposits have been found in different parts of the country [Abdullahi and Audu, 2015]. An estimated reserve of about 7000 million tonnes had been indicated in the north eastern (black cotton soil) part of Nigeria (Salahudeen, Ahmed, Ajinomoh, Hamza and Ohikere, 2012]. These areas comprise of Borno, Adamawa and Taraba State (James, Adwsiran, Adekola, Odebunmi and Aekeye, 2008]. This large bentonite reserve awaits commercial exploration for its various uses.

## EXPERIMENTAL PROCEDURE

Bulk bentonite was first gently ground and separated into fractions with grains smaller than  $2\mu\text{m}$  by centrifugation and sedimentation. Samples of bentonite were air dried at room temperature and later compacted for further experiments. The montmorillonite-rich clay particles of the raw sample presented flat surfaces and a uniform particle size distribution.

### *Bentonite Clay-Based Catalyst Preparation*

Two dioctahedral smectites, extracted from bentonite from Borno and Adamawa States were treated with sulfuric acid of different molarities. Bentonite particles not exceeding  $2\mu\text{m}$  were separated by the decantation method. Typically, 10g of bentonite clay were dispersed in distilled water and left to precipitate for 24hours. A fraction which corresponds to  $2/3$  of the height of the upper limit was separated, centrifuged for 5 minutes at 500 revolutions/minute and left to dry in air.

Such prepared bentonites were labeled MB and MA where M is the molarity of  $\text{H}_2\text{SO}_4$  (1.5MB, 3MB, 4.5MB, 6MB and 1.5MA, 3MA, 4.5MA, 6MA). The untreated bentonites were labelled B (bentonite from Borno) and A (bentonite from Adamawa). For the  $\text{H}_2\text{SO}_4$  acid treatment 5g of previously purified B and A bentonite was separated and dispersed in 50ml of 1.5M, 3M, 4.5M and 6M  $\text{H}_2\text{SO}_4$  (98%). The solid/liquid phase ratio was 1:10. The dispersion was heated for 2hours at  $85^\circ\text{C}$ , centrifuged and flushed with distilled water to a negative reaction to the sulfate ion, which was checked using  $\text{BaCl}_2$ .

The bentonite mineral composition was determined using an X-ray powder diffractometer which is a part of the SIEMENS D500 automated system. The diffractograms were obtained with Cu  $K\alpha = 1.54184 \text{ \AA}$  radiation, with a current of 20 Ma and voltage of 35Kv, with a Ni filter. FT-IR spectra were recorded on a Perkin Elmer model 597 in the  $4000\text{-}400\text{cm}^{-1}$  region using the KBr pellet method (2mg of sample dispersed in 200mg KBr). Chemical



analyses were done using the atomic absorption spectrophotometry method (AASF), by a flame technique, on an AAS 4000 Perkin Elmer and the CEC was determined by ammonium acetate method, pH 7.0. Changes in particle morphology were observed with scanning electron microscope using a JEOL JSM-6610LV connected with an INCA350 energy-dispersion X-ray (EDX).

The specific surface area was determined using the adsorption and desorption nitrogen isotherms, at liquid nitrogen temperature (-196°C). Before measurement, the sample was degassed at 120°C and vacuumed for more than 24 hours. Analysis of results involved the determination of specific surface area of the sample using the BET equation. BaCl<sub>2</sub> test was conducted to ensure the slurry is free of SO<sub>4</sub><sup>-</sup> ions. The resulting acid activated clay was dried overnight at 110°C and ground to a fine powder.

### **Direct Methods for the Preparation of Nano-Particles**

Reduction or hydrolysis in polyols is a versatile method to prepare fine metal or oxide particles. The polyol process, reported in the literature, is a soft chemistry method which allows to prepare oxide or metal nanoparticles with controlled size and shape. The polyol acts as a solvent for the metal precursors (high permittivity), a growth medium and a complexing agent in some cases. In addition, it is also a mild reducing agent. This process permits to tune the particles size, shape, composition and structure of particles via the control of the nucleation and growth steps and, in recent years, it has called a growth attention. With the help of various additives, surfactants (e.g. polyvinylpyrrolidone) and microwave heating, various types of nanoparticles have been synthesized. Metals (Ni, Co, Cu, Pd, Ag, Pt, Au), alloys, oxides (MgO, TiO<sub>2</sub>, ZnO, SnO<sub>2</sub>, Gd<sub>2</sub>O<sub>3</sub>, Fe oxides and ferrite), hydroxyapatite, metal-polymer nano-composites, supported metal catalysts, have been designed (Cortes, Mejfa, Ruiz, Benjumea and Rifel, 2012, Nassar, Hassan and Pereira-Alao, 2011).

### **Fixation of the precursor on the host support, followed by its transformation into the invited phase (oxide or metal)**

In this work, the bentonite clay was impregnated by a solution of Pd (NH<sub>3</sub>)<sub>4</sub> (NO<sub>3</sub>)<sub>2</sub> before calcination in oxygen at 550°C. At low Pd loading, the Pd<sup>2+</sup> ions were isolated and their UV-Visible spectrum shows a d-d transition at 430nm. When increasing the Pd content, the Pd<sup>2+</sup> and oxygen ions from Pd<sub>x</sub>O<sub>y</sub> clusters whose absorption edge, appeared at a higher wave length (about 630 nm) than the d-d transition of isolated Pd<sup>2+</sup> ions and at lower wave length (higher energy) than bulk PdO, a p-type semiconductor (absorption edge near 1700 nm, not shown). The band at 250nm is ascribed to a palladium-oxygen charge transfer. Also, NiO/clay was prepared by the impregnation (incipient





wetness) method with Ni (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O according to literature procedure (Hossain, Al-Saleh, Shalabi, Kimura and Inui, 2004).

### Catalysts and their Characterization

The surface area and porosity characteristics of the calcined catalysts were determined by nitrogen adsorption-desorption isotherms at 77K using a Micromeritics TriStar II 3020 instrument. The adsorption-desorption curves of the isotherms were recorded and the surface area measurements were done according to the BET (Brunauer-Emmett-Teller) method. The pore size distributions were obtained applying the BJH (Barrett, Joyner, Halenda, 1951) method on isotherm desorption branch and the micropores area and volume were obtained applying the t-plot (de Boer) method.

External surface, morphology and structure of catalysts were visualized by Scanning Electron Microscopy (SEM) and the chemical compositions were determined by EDAX (Energy Dispersive Analysis of X-Rays) method using a QUANTA 133 Electron Microscope (FEI Company). Structural information of catalysts were obtained by FTIR spectra registered with a JASCO-FTIR 610 Fourier-transform infrared spectrometer (FTIR) in the 4000-400cm<sup>-1</sup> wavenumber range, using the KBr pellet technique.

In details, the virgin Supports were analyzed using X-ray Fluorescence (XFR) with a Rigaku spectrometer, equipped with a graphite monochromator using CuK $\alpha$  radiation (40kV) and angular domain scanned  $6^{\circ} \leq 2\theta \leq 70^{\circ}$ . N<sub>2</sub> adsorption and desorption experiments at 77K were conducted in an Autosorb-1 from Quantachrome after outgassing samples overnight at 413K. The surface area of the materials was calculated using the Brunauer-Emmett-Teller (BET) method, and the pore size distribution curves were obtained from desorption isotherms by the Barret-Joyner-Halenda (BJH) method. Temperature programmed desorption with NH<sub>3</sub> (TPD-NH<sub>3</sub>) experiments was performed to measure the total acidity of the prepared catalysts with the aim to correlate the surface acidity with the catalytic behaviour in the decomposition tests [Alhawalha, et al., 2011]. Approximately 100mg of each prepared catalysts was dried at 473K for 1 hour under the flow in a U-shaped quartz tube.

Then, a fixed amount of 10 vol% NH<sub>3</sub> in Heat 80mL/min was introduced to be adsorbed at 373K for 1 hour. The carrying gas was changed again to pure He at 80mL/min at 373K for 1 hour and finally heated up to 1143K at 10K/MIN. A calibrated thermal conductivity detector (TCD) with a constant flow of Heat at 80mL/min senses the changes in the flow of the gas through the instrument, due to the desorption of the NH<sub>3</sub> in the heating ramp. The instrument used to TPD-NH<sub>3</sub> experiments was a Chembet 3000 (Quantachrome Instruments, USA). The determination of metal dispersion and average metal particles sizes in supported catalyst were performed by



pulse chemisorption using H<sub>2</sub> titration with the Chembet 3000 (Quantachrome Instruments, USA).

### Heavy Crude Oil Feedstock and Bitumen

The heavy crude oil used in this work, was supplied by the Nigerian National Petroleum Corporation (NNPC) Port-Harcourt Refinery. The properties of the feedstock are presented in Table 1:

**Table 1:** Properties of heavy oil feedstock.

Parameter	Value
API gravity (°)	14.2
Viscosity at 20°C (Pa.s)	1.08
Density at 15°C (g.cm <sup>-3</sup> )	0.98
Sulfur (wt.%)	3.4
Ni (ppm)	55
V (ppm)	148
Ni + V (ppm)	203
Asphaltene (wt.%)	12.2

The dry bitumen was provided by NNPC, Warri Refinery.

*Source:* Experimentation, 2018

### Batch Adsorption Experiments

According to the SARA heavy fraction content (asphaltenes and resins) in the extra heavy oil, the asphaltenes and resins have a mass ratio corresponding to 20:80 respectively in the oil matrix. Hence, batch adsorption experiments were performed at 298 K for different concentrations of a 20:80 mixture of resins and asphaltenes (R-A). The R-A mixtures were added in toluene at concentrations from 100 to 5000 mg/L and for a ratio of the solution volume to the dry mass of catalysts of 10 g/L. The solutions were stirred for 24 hours to ensure the maximum adsorption of the heavy compounds.

Finally, the catalysts with adsorbed heavy compounds were separated from the solutions and dried to remove any traces of solvent. The amount of the heavy fraction in the adsorbed phase was measured by thermogravimetric analyses (TGA) with a Q50 analyzer in (TA Instruments, Inc., New Castle, DE, USA). Thermogravimetric analyses, in this case, were performed under an air flow of 100mL/min with a heating rate of 5K/min from 373 to 1173 K. The differences in the mass loss between the virgin catalysts and catalyst with adsorbed species determine the total amount adsorbed.

### Extraction and Analysis of Asphaltenes in Crude Oil and Products

The Institute of Petroleum of London (Standard Methods for Analysis and Testing of Petroleum and Related Products – vol.1, IP-143) developed a methodology which is a standardized test which consists in the precipitation



of part of the oil with n-heptane and then dissolving the precipitate with toluene. The precipitate is soluble in toluene and is then called asphaltenes. This methodology, as well as its American Version (ASTM 6560-00), are commonly used by the oil industry for the quantification of asphaltenes. The asphaltene fraction of the heavy oil may be recovered by dilution with straight chain alkanes such as n-pentane or n-heptane and recovering the precipitate obtained. The remaining portion thereafter is known as maltene, which consists of a mixture of saturates, aromatics, and resins. In this study, the asphaltene fraction was precipitated from the corresponding feed oils and produced upgraded oils using n-heptane in accordance with the ASTM D2007-80. Specially, 1 gram of the samples was mixed with 40 mL volume of n-heptane, as a precipitant. The mixture of oil and n-heptane was agitated for 4 hours using a magnetic stirrer. Thereafter, the mixture was left for 24 hours to allow the asphaltenes to precipitate and settle. The precipitated fraction was collected and vacuum filtered using a Whatan 1 filter paper with 11  $\mu\text{m}$  pore size and 4.25 cm diameter to separate the n-heptane soluble portion (i.e., maltene) from the asphaltene portion (i.e., n-heptane insoluble). The filtered asphaltenes were washed with n-heptane until a colourless liquid was observed from the filter. The filter paper and precipitate were dried under an inert gas flow for 24 h to remove any residual n-heptane, and then the precipitated asphaltenes were weighed.

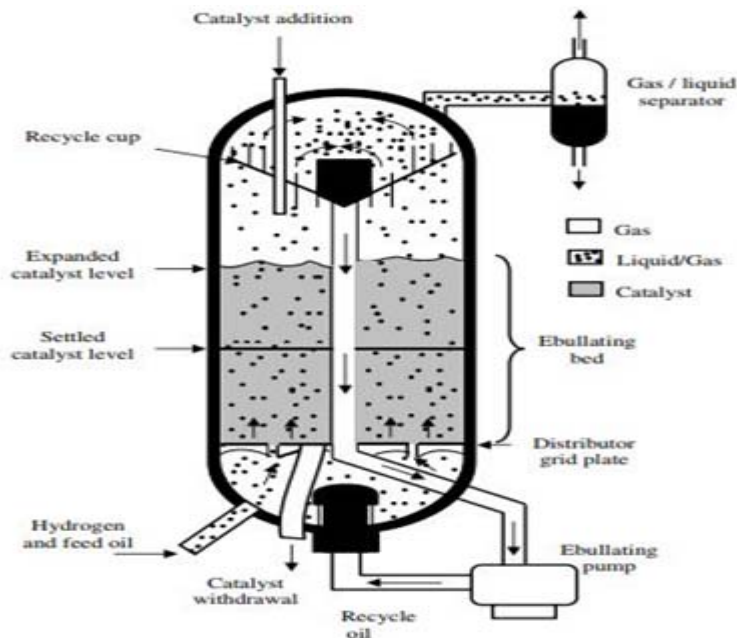
### Catalyst Evaluation

Small-scale testing of heterogeneous catalysts plays an important role during the development of a catalyst, especially at the early stages. Several types of small-scale catalyst test reactors, such as the differential reactor and the micro-reactor or isothermal integral reactor, are available. The choice of a particular reactor depends on the detailed objective should also be considered. Basic kinetic experiments are carried out using differential reactors, while integral reactors allow a high degree of conversion, which is suitable for realistic evaluations on a large scale. To obtain information on all aspects of a process, more than one type of reactor is needed. The hydro conversion plants that use supported catalysts can be divided into two categories, based on the technology used: those with fixed bed reactors. Its extreme sensitivity to high concentrations of poisons makes fixed bed technology particularly suitable for treating the atmospheric residues from conventional crudes, but not suitable for feedstocks produced from non-conventional oils.

Unlike fixed bed technology, ebullated bed technology is suitable for treating feedstocks with a high content of contaminants and, as such, is used to process vacuum residues even from particularly heavy feedstock. Furthermore, this solution displays a high degree of flexibility for feedstocks coming from different crudes, provides almost constant yields and product

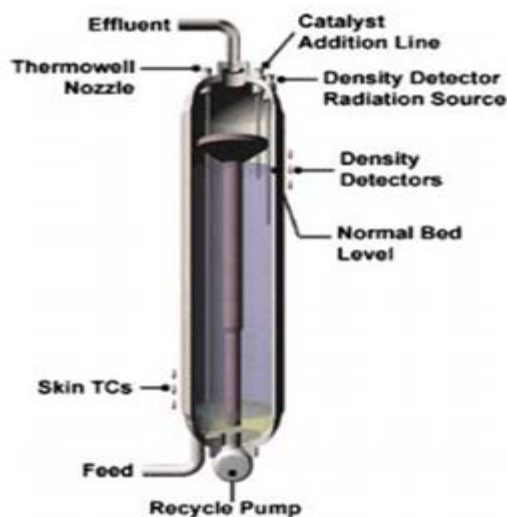


quality, and has high operational flexibility. There are two most important ebullated bed processes, which are similar in concept but different in mechanical details that are given below.



**Figure 4:** Schematic representation of the H-Oil reactor, IFP.

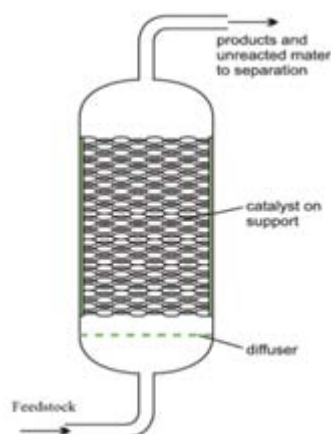
*Adapted from:* Colyar JJ, Wisdom LI. *Upgrading vacuum residue from Mexican crudes for petroleos Mexicanos hydrodesulfurization residue complex Miguel Hidalgo Refinery. Tokyo (Japan): Japan Petroleum Institute; 1992.*



**Figure 5:** LC-Fining reactor.

*Adapted from:* Daniel Mc, Lerman DB, Peck LB, Amoscós LC-fining residue hydrocracking yield and performance correlations from a commercial unit. NPRA, 1988.

The general advantages of LC-finishing are: low investment, more light-ends recovery and lower operating costs. This process yields a full range of high quality distillates; heavy residue can be used as fuel oil, synthetic crude, or feedstock for a resid FCC, coke, visbreaker or solvent deasphalter (Rana, Samano, Ancheyta and Diaz 2007; *Fuel*, 86(9) 1263–1269, 2007a).



**Fig. 6:** Fixed-bed reactor

Laboratory-scale experiments were conducted in a fixed bed micro-reactor, using conditions shown in **Table 2**.

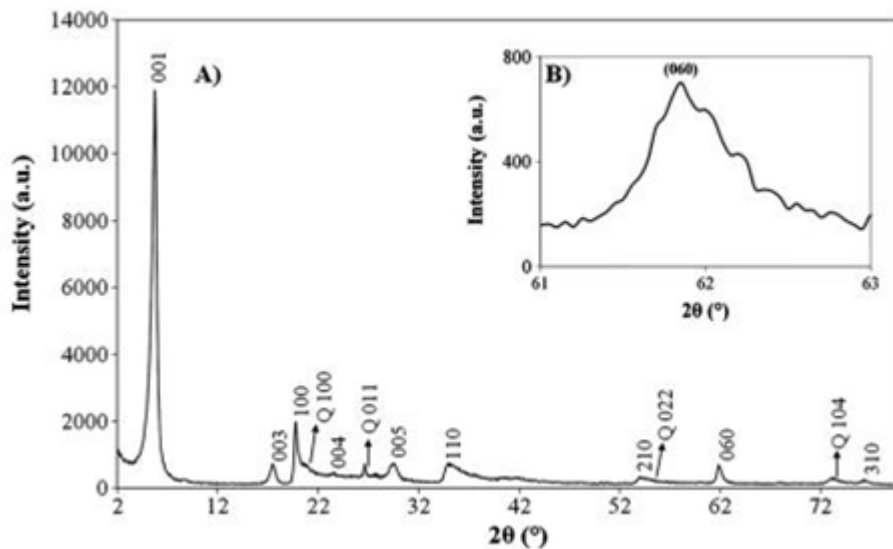
**Table 2:** Experimental conditions.

Parameter	Values
Catalyst weight (g)	7
Feedstock weight (g)	65
Catalyst-to-oil (CTO) ratio	0.2
Residence time (minutes)	15
Reaction temperature (°C)	425
Reynolds number	0.195
Pressure (bar)	20
Agitation (rpm)	-
Oil flow rate (mL min <sup>-1</sup> )	1±0.2
Reaction atmosphere	N <sub>2</sub>

## RESULTS AND DISCUSSION

**Bentonite clays: X-ray diffraction analysis:** XRD pattern of the bulk bentonite showed mainly smectite characterized by the 001 reflection and minor impurities of quartz (Fig. 7A). XRD analyses of air-dried samples (powder diffraction) presented the characteristics reflections corresponding to d values

of 15.4Å (001), 5.1Å (003), 3.8Å (004) and 3.0Å (005), which were in agreement with the basal values for smectites (Table 3) (Greene-Kelly, 1953; Rosenquist, 1959; Bergaya, Theng, Lagaly, 2006). The b-parameter (from the 060 reflection) at 1.50Å (Fig. 7B) corresponds to a dioctahedral smectite in which the high intensity of  $d_{060}$  reflection indicated a large size of the coherent domains along the b direction (Calarge 2001; Calarge, Meunier and Formoso, 2003).



**Fig. 7.** A) X-ray diffraction pattern of bulk bentonite (air dried-random powder AD) and Miller indexes (Table 3), B) (060) reflection at 1.50Å.

**Table 3:** Miller indexes and values of the montmorillonite (B1) and the typical XRD patterns of montmorillonite (Rosenquist, 1959)

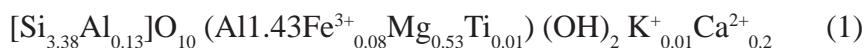
Miller Index	(001)	(003)	(100)	(004)	(005)	(110)	(210)	(060)	(310)
$D$ (Å)	15.00	5.01	4.50	3.77	3.02	2.58	1.70	1.50	1.24
$D$ (Å)-B1	15.36	5.08	4.49	3.77	3.02	2.57	1.70	1.50	1.24

Thermogravimetric analyses (TGA) were carried out on a Shimadzu system model TGA-50 from room temperature (RT) to 800°C for the TGA/TDA analyses and to 1000°C for measuring the loss of ignition, using a heating rate 20°C/min in argon atmosphere.

### Chemical Composition

The bulk bentonite chemical composition (Table 3) determined by XRF, showed high contents of silicon and CaO. The structural formula calculated for the smectite (equation 1) content of bulk bentonite was determined by XRF, and was in agreement with the calcium montmorillonite compositions as the predominant phase in the bentonite sample. The montmorillonite content in bentonite determined was calculated by XRD analyses of Greene-Kelly (1953)

and presents minor impurities of quartz. Calcium was the main interlayer cation of montmorillonite and the sum of the exchangeable ions ( $\text{Ca}^{2+}$ ,  $\text{K}^+$ ) of 0.47 per half formula unit indicated a high-charge smectite.



The specific surface area of the bulk bentonite measured by BET was  $67\text{m}^2/\text{g}$ . Chemical analyses of the bulk samples were performed by X-ray fluorescence (XRF). The loss on ignition was measured by thermogravimetry.

**Table 4:** Chemical composition of the bulk bentonite (in mass %).

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{MnO}$	$\text{MgO}$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{TiO}_2$	$\text{P}_2\text{O}_5$	LOI	Total
59.69	21.23	1.71	0.14	5.89	3.02	Nd	0.29	0.31	0.02	7.66	99.96

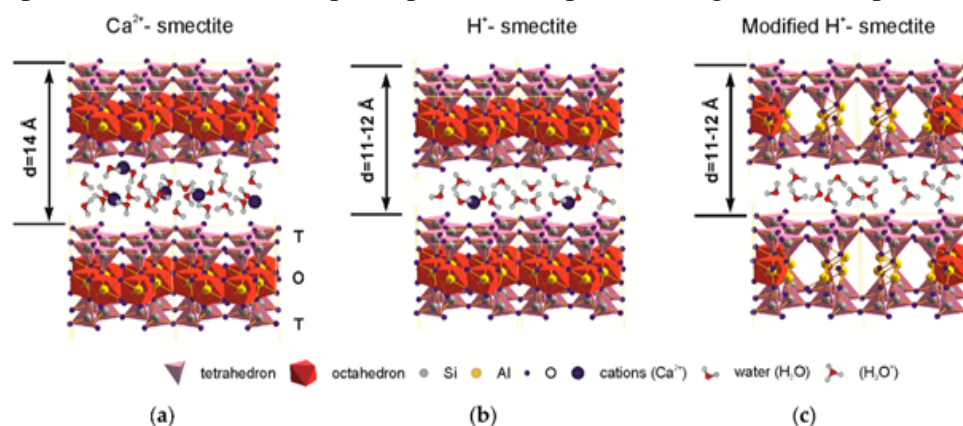
\*Nd: not detected

\*LOI: loss on ignition at  $1000^\circ\text{C}$ . Source: Experimentation, 2018

### Transformation of the Montmorillonite Structure under Acid Treatment

Considerable crystal-chemical transformations-in particular, changes of montmorillonite micromorphology and adsorption characteristics were observed during the treatment with inorganic acid solutions.

Protonation of Al bond pair in the octahedron transforms it from 4-coordination to 6-coordination and leads to the modification of octahedral and tetrahedral sheets and to an appearance of microspores simultaneously decreasing the number of octahedral cations. Changes in the layer stacking and particles' micromorphology results in mesopore formation. Structural transformations are shown simplified in Figure 8. Thus, there is an increase of specific surface area and pore space both capable of large cation sorption.



**Figure 8.** Schematic picture representing the structural changes in natural montmorillonite under the treatment with inorganic acid solutions: (a) natural Ca-montmorillonite; (b) partial protonation of interlayer space; (c) full protonation of interlayer space (H-smectite) and protonation of the OH-groups of the octahedral sheet and Al coordination change (Krupskaya et al., 2017)

The nitrogen adsorption-desorption isotherms are predominantly type I (Langmuir) combined with type IV Isotherm, according to International Union of Pure and Applied Chemistry (IUPAC) classification (Krupskaya, *et al.*, 2017). The adsorption isotherms suggest that the acid-treated montmorillonites are meso- and macroporous materials. Table 5 presents the surface area and porosity characteristics and the pore size cumulative derived distribution curves (pore volume, pore area) of the studied catalysts supports.

**Table 5:** Surface area and porosity characteristics of studied catalysts supports

Bentonite Clay Source	Specific surface area, BET <sup>a</sup> , [m <sup>2</sup> .g <sup>-1</sup> ]	Microspores area <sup>b</sup> , [m <sup>2</sup> .g <sup>-1</sup> ]	Micropore volume <sup>b</sup> , [cm <sup>3</sup> .g <sup>-1</sup> ]	Meso- & macropores area <sup>c</sup> , [m <sup>2</sup> .g <sup>-1</sup> ]	Meso- & macropores volume <sup>c</sup> , [cm <sup>3</sup> .g <sup>-1</sup> ]	Average meso- & macropores diameter <sup>c</sup> , [Å]
<i>Borno State</i>	27.80	9.48	0.0013	28.32	0.108	153
<i>Adamawa State</i>	18.26	5.70	0.0003	20.57	0.081	157

<sup>a</sup>BET method; <sup>b</sup>t-plot method; <sup>c</sup>BJH desorption method.

**Source:** Experimentation, 2018.

The surface area is the measure of the catalyst activity of the same catalyst types and has a strong effect on the performance of catalytic process. Thus, the Borno State clay catalysts support has highest value of BET surface area of 27.80m<sup>2</sup>.g<sup>-1</sup> and the value of meso- and macropore volume of 0.108cm<sup>3</sup>.g<sup>-1</sup>. The Adamawa State clay catalyst support has BET surface area and meso- and macropore volume of 18.26m<sup>2</sup>.g<sup>-1</sup> and 0.081cm<sup>3</sup>.g<sup>-1</sup> respectively. The average pores diaeter is 153Å for Borno State clay catalyst and 157Å for Adamawa State clay catalyst and suggests a large number of macropores. There are small differences in pore distribution for both catalyst supports.

### Functionalization of Acid-Modified Montmorillonite

**Table 6:** Specific surface area, total acidity, mean crystallite size and metal dispersion for functionalized bentonite clay and non-functionalized clay.

Sample	S <sub>BET</sub> ± 0.1 m <sup>2</sup> /g	Total Acidity ± 0.02 µmol/g	Mean Particles Size of Active Phase ± 0.1 nm	Dispersion (%)
<i>Bentonite Clay</i>	19.6	376.02	-	-
<i>PdO/bentonite clay</i>	15.1	161.24	8.9	20
<i>NiO/bentonite clay</i>	14.3	127.41	13.5	15

**Source:** Experimentation, 2018

TPD-NH<sub>3</sub> profiles of ammonia desorption for clay, and the functionalization results of total acidity are listed in Table 6. The TPD profile obtained with the adsorption/desorption of NH<sub>3</sub> molecules in the samples gives information related to the type of acidity present in the sample based on the desorption peaks. In a previous study, the results of which have been reported elsewhere (Rodriguez, Beltran, Vazquez-Labastida, Linares-Lopez Salmon, 2007), two predominant peaks at 590K and 845K for fresh clay were observed





due to the presence of Lewis and Bronsted sites. The low-temperature peak observed in a TPD profile is related to the Lewis sites. Furthermore, the high-temperature peak is associated with the Bronsted sites, because the energy required to promote the  $\text{NH}_3$  desorption is higher. Pulse  $\text{H}_2$  chemisorption measured the covered metal surface after functionalization process to identify the formation of metal oxide nanoparticles through the  $\text{H}_2$  consumption. Results of the metal oxide mean particle size for the studied samples are shown in Table 6 above. The obtained results confirm the formation of metal oxide nanoparticles over the support surface. Also, when comparing the PdO-containing materials with that of NiO, it is observed that PdO/clay offers a higher acidity than NiO-containing materials.

### Adsorption Isotherms of Resins and Asphaltenes

Due to the high molecular weight of the heavy fractions compounds, the diffusion of these molecules through the pores in a porous materials is low. For this reason, textural properties such the volume and pore diameter are more important in the heavy fraction adsorption than the specific surface area of the material. In accordance with the International Union of Pure and Applied Chemistry (IUPAC), the obtained adsorption isotherms follow a Type Ib behaviour, which means a strong interaction between the available active zones in the adsorbent and the R-A mixture (Cortes, *et al.*, 2012; Hosseinpour, Khodadadi, Bahramian and Mortazavi, 2013). However, the asphaltenes-resins interactions and a lower amount of functional groups, as well as low polarity in resins structure, could affect the interactions between the adsorbent and adsorbate. The low asphaltenes concentration and the colloidal state of the adsorbate affects the asphaltene-asphaltene interactions, indicating that the adsorption process could be governed by the interaction of the adsorbent with the asphaltene-surrounding resins.

A suitable catalyst for the heavy fraction adsorption by longer pores and higher surface acidity results in a better adsorptive behaviour. In addition, a higher acidity in the active sites generates an improvement in the affinity between the adsorbate and the adsorbent. For PdO/Montmorillonite and NiO/Montmorillonite materials, a higher total acidity could lead to a strong adsorption process, due to the relation between the adsorption affinity (i.e.,  $H$  lower) and the total acidity reported in Table 6. Nassar, Hassan, Pereira-Alao (2011) and Franco *et al.* (2015) show that relationship exists between the surface acidity and the adsorption capacity of asphaltenes. Attraction forces between the O- and N-containing functional groups of the heavy fraction with active sites available for the adsorption process is expected to be an important adsorption mechanism. The high clay acidity is associated with a better diffusion of  $\text{NH}_3$  molecules through the pores of the particle due to their low



particle diameter. However, the available acid sites for heavy fraction adsorption is less, due to the aggregates formed in the R-A systems that decrease the diffusion capacity through the porous materials. It has been reported that the addition of resins to asphaltene solutions changes the self-aggregation of the asphaltenes. The stabilization effect of resins has been attributed to form smaller structures preventing the flocculation of the asphaltenes particles. Spiecker *et al.*, (2014) found that with an R-A ratio of about 10.1 in toluene solutions, R-A aggregates correlated a length between 11-14Å. This indicates that the active acid sites where the adsorption could happen are less than the total acid sites of the particle. In this sense, a surface impregnation with the metal oxide leads to active sites that are more available for R-A adsorption.

**Table 7:** Catalytic activity in hydrocracking [Conversion of Asphaltenes selectivity to maltenes (%), in an autoclave reactor]

<i>T(k)</i>	Asphaltene conversion, %Catalyst System		
	Acid-modified Montorillonite	NiO/MMT	PdO/MMT
473	66.3	77.6	88.1
523	68.4	91.7	94.5
573	69.2	93.8	96.3

Reaction conditions:

- Hydrogen pressure = 1.0 Mpa
- Reaction time = 1 hour
- Concentration of Catalyst = 3wt.%
- Asphaltene content = 10.3 wt.%

The data in Table 7 indicate considerable catalytic activity in hydrocracking of asphaltenes. The differences in the sample chemical compositions and surface characteristics are responsible for different catalyst activity in reactions of hydrocarbon conversion of petroleum components (hydrocracking of heavy components- asphaltenes). Heavy oil fractions conversion was enhanced by the presence of metal oxide nanoparticles as active materials.

### Asphaltenes, Sulfur and Metals Content

The asphaltene content of the heavy oil contributes very significantly to its high viscosity, low API gravity and low fuel distillates fractions. The sulfur and metals impurities are mostly concentrated in the macromolecules of the resins and asphaltenes. Hence, their reduction is an essential goal of catalytic upgrading, in order to improve API gravity and viscosity of the oil. Table 8 shows the asphaltene, sulfur and metals content of the feed and upgraded oils. Clearly, as the reaction temperature increases from 350 to 425°C the conversion of asphaltene to low molecular weight components was favoured. The asphaltene content decreased with increase in temperature.



The removal of sulfur and metals is consistent with the conversion of the asphaltene. This shows that reaction temperature plays a significant role in cracking the macromolecules such as resins and asphaltenes that incorporate the sulfur and metals in order for them to be removed. The asphaltene content before and after the upgrading reactions was determined through precipitation using  $n\text{-C}_7\text{H}_{16}$ .

**Table 8:** Asphaltenes, sulfur and metals content before and after reactions.

Impurities	Heavy oil	After reaction (350°C)	After reaction (400°C)	After reaction (425°C)
Asphaltene (wt.%)	12.2	7.31	6.18	5.48
Sulfur (wt.%)	3.4	2.9	2.7	2.4
Nickel (ppm)	55	49	46	4.3
Vanadium (ppm)	148	138	133	129
Ni + V (ppm)	203	199	193	182

\*Note Sulfur and metals content was performed using ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry).

Source: Experimentation, 2018

The asphaltene content of crude oil confers high viscosity and low API gravity. The presence of heteroatoms (e.g., N, S) and metalloporphyrins of nickel, vanadium, iron, etc. are known to impact on downstream refining processes and catalysts. In Table 8 the asphaltene, metals and sulphur contents before and after upgrading clearly, the asphaltene content after upgrading decreased. One of the main purposes of upgrading the heavy crude oil is to make it easily refined by conventional refinery methods, and also increase the amount of more valuable light distillates.

This study evaluated the supports and active phase nature by the employment of bentonite clay materials as support of NiO and PdO active phases in the catalytic cracking of the heavy compounds of the crude oil. Structural properties such as the pore size distribution and the total acidity of the materials impact on the adsorption and subsequent catalytic cracking of the heavy species. Pore size distribution defines the aggregates that could be adsorbed and the sites that would interact with the heavy fractions.

Also, available acid sites are responsible for the adsorptive and catalytic capacity of the minerals. Acid-modified bentonite structure for heavy molecules adsorption due to the presence of larger pores in comparison with unmodified clay structure. Although clay presents a higher total acidity, the degree of heavy molecules diffusion through clay structure is a function of the average size of the aggregates. The presence of metal oxide nanoparticles enhanced the R-A adsorption by the formation of a heterogeneous adsorbent with various selectivity for the heavy fraction that is more efficient in attracting heavy compounds to the catalyst surface. An improvement in the catalytic behaviour

could be achieved with the functionalization process. The potential application of metal oxide nanoparticles as an alternative to the current techniques in heavy oil upgrading could lead to the employment of materials with different surface nature for heavy fractions adsorption and subsequent catalytic decomposition at relatively low temperatures. In this sense, various commercial and synthesized metal oxides show high capacity and affinity for asphaltene adsorption and decomposition. Due to the low cost of the mesoporous materials, textural properties modification like pore size and surface area are used to improve the adsorptive capacity. The active phase comprises metal oxides on the support surface. The clay most widely used as an efficient solid acid catalyst is 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. The acid-modified montmorillonite find diverse applications as catalysts, catalytic support and adsorbents. The acid-modified montmorillonite catalysts are widely studied in petroleum cracking. The combination of acid-modification and functionalization provides a potential enhancement of the clay properties for application in upgrading heavy crude oil and bitumen.

**Table 9:** Hydro-desulfurization Reactions of Bitumen with PdO/MMT.

Catalyst	Substrate	Time, Hr	Sulfur in Substrate, <sup>b</sup> %	Sulfur in Product, %	Sulfur Removed, %
3wt. %	Dry Bitumen	1	4.9	3.3	87
6wt. %	Dry Bitumen	1	4.9	3.3	93

<sup>a</sup> = Ratio is based on the dry weight of bitumen.

<sup>b</sup> = present sulfur is based on the dry weight of bitumen.

*Source:* Experimentation, 2018

**Table 10:** Hydro-desulfurization Reactions of Bitumen with NiO/MMT Catalyst

Catalyst	Substrate	Time, hr	Sulfur in Substrate, <sup>b</sup> %	Sulfur in Product, %	Sulfur Removed, %
3wt. %	Dry Bitumen	3	4.6	3.2	69
6wt. %	Dry Bitumen	3	4.6	3.2	75

<sup>a</sup> = Ratio is based on the dry weight of bitumen contained.

<sup>b</sup> = present sulfur is based on the dry weight of bitumen.

**MMT** = Montmorillonite. – *Source:* Experimentation, 2018

Palladium based catalysts are known for their high hydrogenation activity, and may suppress coke formation. Further, literature survey shows that Pd can promote hydrodesulfurization. This can be observed when tables 9 and 10 are compared.



**Table 11:** Effect of functionalization on Upgrading of heavy crude oil.

Catalyst (wt.% of feed oil)	Conversion, (%) Liquid (wt.% of feed oil)	Coke (wt.% of feed oil)	Gas
Acidified bentonite	59.7	7.1	8.05
PdO/bentonite	96.4	1.86	3.34
NiO/bentonite	88.3	12.07	7.88
			7.85
			93.8
			80.05

**Experimental conditions:**

- Temperature: 343°C;
- Catalyst loading; 6wt.%.

**Source:** Experimentation, 2018

The quantitative and qualitative data showing the extent of upgrading of the heavy oil are presented in Table 11. Heavy oil and bitumen are viewed as a large potential energy sources since their total reserve of about 9-13 trillion barrels out-weighs conventional light crude oil reserves of about 1.02 trillion barrels. Heavy oil and bitumen contain resins and asphaltenes which give them the characteristics of high viscosity, high density/low API gravity, high metals and heteroatom content. Upgrading therefore improves refineability; reduces metals and heteroatom content as coke precursors such as resins and asphaltenes are converted into valuable liquid products.

**Table 12:** Effect of functionalization on Coke Formation

S/No	Catalyst (3wt.%)	Coke, wt.%
1.	Raw bentonite	-
2.	Acidified bentonite	32.74
3.	NiO/bentonite	18.16
4.	PdO/bentonite	12.83

**Source:** Experimentation, 2018

The amount of coke produced from cracking of the heavy oil was determined using thermogravimetric analysis (TGA) of the deposit after upgrading. The distribution of liquid (i.e., upgrading oil), gas, and coke products after upgrading was calculated as the yield from the weight of heavy oil fed into the reactor using Equations 2 and 3:

$$\text{Yield of product (wt.\%)} = \frac{W_i}{W_{\text{feed}}} \times 100 \quad (2)$$

$$\text{Gas (wt.\%)} = 100 - \text{liquid yield (wt.\%)} - \text{coke yield (wt.\%)} \quad (3)$$

Where  $W_i$  is the weight of product  $i$  (i.e., gas, upgraded oil and coke)

And  $W_{\text{feed}}$  is the overall weight of the feed oil.

The amount of coke was determined from the TGA of the recovered deposits in the reactor after the upgraded oil sample was collected. The burn-off of coke occurs at temperatures beyond that of n-heptane separated asphaltene, because the deposit is a composite of residual oil, polar



macromolecules such as resins and asphaltenes, and coke. It can be seen that the  $nC_{7}H_{16}$ - separated asphaltenes burn-off completely as the temperature increases from 430 to 640°C. It has been reported for coked catalyst after upgrading that the burn-off beyond that of asphaltenes can be regarded as hard coke. Therefore, the portion of the deposit that is coke after reactions with the different particulate catalysts is as presented in Table 12, hence, PdO supported on acidified bentonite produces less coke than the NiO supported on bentonite.

The products of the upgrading reaction consist of liquid (i.e., light oil), gas and coke. The produced gas was analyzed using gas chromatography (GC). The liquid product (i.e., upgraded oil) was collected; thereafter measurements of viscosity, API gravity, and simulated distillation by GC using ATSM D2887 method. The expression used to calculate the conversion of heavy hydrocarbons (HC) with boiling above 343°C is given by Equation (4). The conversion definition does not take into account carbonaceous deposits on the catalysts or reactor as unconverted feed.

$$\text{Conversion} = \frac{(343^{\circ}\text{C})\text{HC in feed} - (343^{\circ}\text{C})\text{HC in products}}{(343^{\circ}\text{C})\text{HC in feed}} \quad (4)$$

## CONCLUSION

The surface of inorganic clay bentonite was modified by acid treatment and the surface modification was confirmed by characterization using FTIR and TGA. Surface modified bentonite clay was used as catalyst support which was functionalized using metal oxide nanoparticles. Catalysis is one of the important tools for sustainability and profitability of chemical product processes. Therefore, the rational design and preparation of novel catalysts based on clay minerals has received much concern over the past four decades.

Modified clay minerals have been identified as important alternative for the generation of materials with potential applications in catalysis, either as catalysts or catalyst supports, due to their low cost and abundance. Their physicochemical and mechanical properties allow a very wide range of possibilities for structural, textural and chemical modifications. Many conventional catalysts applied in petroleum refining industry are derived from oxides of an element belonging to group VIB or group VIII supported or impregnated on different materials such as alumina and clay. The structure, 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, selectivity, high density, surface area, porosity and thermal stability.

The potential application of metal oxide nanoparticles as an alternative to the current techniques in heavy oil upgrading could lead to the employment of materials with different surface nature for heavy fractions adsorption and subsequent catalytic decomposition at relatively low temperatures. In this context, this work focused on the evaluation of bentonite clays obtained from north-eastern Nigeria, functionalized with nanoparticles of metal oxides and their effects on the decomposition of heavy fractions of crude oil such as resins and asphaltenes. The decomposition of the heavy fractions of crude oils is achieved at relatively low temperatures aiming at the early upgrading of heavy and extra-heavy oils. Nanoparticles of metal oxides supported on bentonite clay improved the efficiency of hydrocarbon conversion, reduce or even eliminate catalyst poisoning issue, and provide better refining efficiency for extra heavy and sour crude oils.

The experimental data support the hypothesis about the feasibility of catalytic reactions in oil beds using natural materials (bentonite clays). The reported results are considered to be the basis for future studies of mineral matrices in the development of effective catalysts for in-situ treatment of heavy hydrocarbons in oil industry. This study opens a wider landscape about the use of nanoparticle-functionalized catalysts for the production and transport of heavy and extra-heavy crude oils. The catalyst comprises of an active phase supported on a macro or mesoporous material. It was observed that the adsorption and subsequent cracking of adsorbed asphaltenes could be improved by the incorporation of 3wt % of NiO and PdO nanoparticles into mesoporous-macroporous bentonite clay in comparison with the NiO-free and PdO-free bentonite clay.

The availability and reduced cost of mesoporous-macroporous materials as bentonite clay, and its adsorptive affinity towards polar hydrocarbons is a cause of interest in the applications as supports of metal oxide nano-catalyst. In this sense, the heavy oil upgrading on surface conditions require catalysts with high and stable activity through heavy oil decomposition at high temperature, good resistance to coke, sulphur compounds, and heavy metals deposition. A correlation between the adsorptive process and the catalytic activity of the nanoparticle-functionalized materials based on affinity, self-association of the adsorbate and effective activation energy is reported. The adsorption behaviour of the crude oil heavy compounds was correlated with the catalytic activity of the functionalized acid-modified bentonite clays.



## REFERENCES

- Abdullahi, S.L** and **Audu, A. A.** (2015). Assesment of Physicochemical Properties of Clays samples obtained from Ashaka, Potisikum and Toungo (Nigeria) and a commercial bentonite from Kofar Ruwa Market, Kano. Proceedings of 1st Annual International Conference, Faculty of Science, Northwest University, Kano-Nigeria (ISBN-978-978-53550-5-5).
- AlShawalha, Roessner, F.; Novikova, L.; Bel'chinskaya, L.** (2011). Acidity of different Jordanian Clays characterized by TPD-NH<sub>3</sub> AND mboh Conversion. *Wolrd Acad. Sci. Eng. Tecnology*, 5, 7-29.
- Ancheyta J., Centeno G., Trejo F. and Marroquin G.** (2003). Changes in asphaltene properties during hydrotreating of heavy crudes. *Energy Fuels* 17, 1233-1238.
- Barrett, E.P.; Joyner, L.G. and Halenda, P.P.** (1951). The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J. Am. Chem. Soc.* 73, 373-380.
- Bergaya F., Theng B.K.G. and Lagaly G.** (2006). Handbook of clay science. Developments in Clay Science, Volume 1. Elsevier Science, Amsterdam.
- Calarge, L. M.** (2001). Estudo mineralógico e geoquímico de bentonitas do sul da Bacia do Paraná (Aceguá, Brasil e Melo Uruguai). Ph.D. thesis, UFRGS, Porto Alegre, Brasil
- Calarge, L., Meunier, A., Formoso, M. L.** (2003). A bentonite bed in the Aceguá (RS, Brazil) and Melo (Uruguay) areas: a highly crystallized montmorillonite. *Journal of South American Earth Sciences* 16, 187-198.
- Colyar J. J. and Wisdom L. I.** (1992). Upgrading vacuum residue from Mexican crudes for petroleos Mexicanos hydrodesulfurization residue complex Miguel Hidalgo Refinery. Tokyo (Japan): Japan Petroleum Institute.
- Clementz, D.M.** (1976). Interaction of petroleum heavy ends with montmorillonite. *Clays Clay Miner.* 24, 312-319.
- Cortes, F.B.; Mejfa, J.M.; Ruiz, M.A.; Benjumea, P.; Rifel, D.B.** (2012). Sorption of asphaltenes onto nanoparticles of nickel oxide supported on nano-particulated silica gel. *Energy Fuels*, 26, 1725-1730.
- Contreras, J.L.; Fuentes, G.A.** (2013). ChemInform Abstract: Sintering of Supported Metal Catalysts. *ChemInform*, 44.
- Daniel Mc, Lerman DB, Peck LB and Amoscós LC** (1988). -fining residue hydrocracking yield and performance correlations from a commercial unit. NPRA
- Encyclopedia of hydrocarbons Vol.III/NEW Developments: Energy, Transport, Sustainability.**





- Furimsky, E.** (2007). Catalyst for upgrading heavy petroleum feeds (Elsevier Science B.V., Amsterdam,
- Figueras, F.** (1988). Pillared clays as catalysts. *Catalysis Reviews – Science and Engineering*, 30457-499.
- Franco C. A.; Lozano M.M.; Acevedo S.; Nassar N.N. and Cortes F.B.** (2015). Effects of Resin Ion Asphaltene Adsorption onto Nanoparticles: A novel Method for Obtaining Asphaltenes/Resin Isotherms. *Energy Fuels*, 30 264-272.
- Fukuyama, H.; Nakamura, T.T. and Ikeda, A.** (2010). Partial Upgrading of Bitumen at Sagd Wellsite. In Proceedings of the Canadian Unconventional Resources and *International Petroleum Conference, Calgary, AB, Canada, 19-21 October.*
- Ghanavati M., Ahmad Ramazani S. A. and Mohammad-Javad S.** (2013). Effects of asphaltene content and temperature on viscosity of Iranian heavy crude oil: Experimental and modeling study. *Energy fuels*, 27, 7217-7232.
- Gonzalez, F., Pesquera, C., Benito, I., Herrero, E., Pocio, C., Casuscelli, S.,** (1999). Pillared clays: catalytic evaluation in heavy oil cracking using a micro-activity test. *Applied Catalysis A: General* 181, 71-76.
- Greene-Kelly, R.** (1953). The identification of montmorillonoids in clays. *Journal of soil science* 4, 233–237.
- Groena J. C., Peffera, L. A.A. and Pérez-Rami´rez J.** (2003). Pore Size Determination in Modified Micro- and Mesoporous Materials. Pitfalls and Limitations in Gas Adsorption Data Analysis. Microporous and Mesoporous Materials. 60. 1-17. 10.1016/S1387-1811(03)00339-1.
- Groenzin, H. and Mullins, O.C.** (1999). Asphaltene Molecular Size and Structure. *J. Phys. Chem. A*, Vol.103, No.50. 11237-11245.
- Hart A., Shah A., Leeke G., Greaves M. and Wood, J.** (2013). Optimization of the CAPRI process for heavy oil upgrading: effect of hydrogen and guard bed. *Ind. Eng. Chem. Res.* 52(44), 15394-15406.
- Hart A., Leeke G., Greaves M. and Wood J.** (2014). Down-hole heavy crude oil upgrading by CAPRI: Effect of hydrogen and methane gases upon upgrading and coke formation. *Fuel* 119 226-235.
- Hassan, S.W.; Ghannam, M. T. and Esmail, N.** (2010). Heavy crude oil viscosity reduction and rheology for pipeline transportation. *Fuel*, 89, 1095-110.
- Hasan, S. W., M. T. Ghannam and N. Esmail** (2010). Heavy crude oil viscosity reduction and rheology for pipeline transportation. *Fuel*, 89(5): 1095-1100.
- Hassan, A.; Lopez-Linares, F.; Nasar, N.N.; Carbognani-Arambarri, L. and Pereira-Almao, P.** (2013). Development of a support for a NiO



catalyst for selective adsorption and post-adsorption catalytic steam gasification of thermally converted asphaltenes. *Catal. Today*, 207, 112-118.

**Hasem, R.; Nassar, N.N. and Almao, P.P.** (2014). Nanoparticle technology for heavy oil in-situ upgrading and recovery enhancement: Opportunities and challenges. *Appl. Energy*, 133, 374-387.

**Hosseinpour N.; Khodadadi A. A.; Bahramian A. and Mortazavi, Y.** (2013). Asphaltene adsorption onto acidic/basic metal oxide nanoparticles towards in situ upgrading of reservoir oils by nanotechnology. *Langmuir*, 29 (46), 14135-46

**Hossain M.M., Al-Saleh M.A., Shalabi M.A., Kimura T. and Inui T.** (2004). Thiophene hydrodesulfurization over noble metal modified Co-clay catalysts. *Applied Catalysis A: General*, 274(1-2), 43-48.

**James O.O., Adwsiran, M.M., Adekola, F.A., Odebunmi, E.O and Aekeye, J.I.D.** (2008); Bentonite from North-Eastern Nigeria. *Journal of the North Carolina Academy of Science*. 124 (4): 154-158.

**Krupskaya V. V., Zakusin S. V., Tyupina E. A., Dorzhieva O. V., Zhukhlistov A. P., Belousov P. E. and Timofeeva M. N.** (2017). Experimental study of montmorillonite structure and transformation of its properties under treatment with inorganic Acid solutions; *Minerals*, 7, 49.

**Laszlo, P.** (1987). Chemical reaction on clays. *Science* 235, 1473-1477

**Laszlo, P.** (1990). Catalysis of organic reactions by inorganic solids. *Pure & Appl. Chem.* 62, 2027-2030.

**Liu D, Li Z, Fu Y, Zhang Y, Gao P, Dai C, et al.** (2013). Investigation as asphaltene structures during Venezuela heavy oil hydrocracking under various hydrogen pressures. *Energy Fuels*, 27:3692-8.

**Lopez-Linares, F.; Nassar, N.N.; Carbognani-Arambarri, L. and Pereira-Almao, P.** (2013). Development of a support for NiO catalyst for selective adsorption and post-adsorption catalytic steam gasification of thermally converted Asphaltenes. *Catal. Today*, 207, 112-118.

**Maity SK, Blanco E, Ancheyta J, Alonso F and Fukuyama H.** (2012). Early stage deactivation of heavy crude oil hydro-processing catalysts. *Fuel* 100:17-23.

**Martins, G.; Berlier, G.; Bisio, C.; Coluccia, S.; Pastore, H.; Marchese, L.** Quantification of Bronsted acid sites in microporous catalyst by a combined FTIR and NH<sub>3</sub>-TPD study. *J. Phys. Chem. C* **2008**, 112, 7193-7200.

**Nassar, N.N.; Hassan, A.; Pereira-Alao, P.** (2011). Application of nanotechnology for heavy oil upgrading: catalytic steam gasification/cracking of Asphaltenes. *Energy Fuels* 25, 1566-1570.



- Nguyen-Huy, C. and Shin, E.W.** (2016). Hierarchical macro-mesoporous  $\text{Al}_2\text{O}_3$ -supported NiK catalyst for steam catalytic cracking of vacuum residue. *Fuel*, 169, 1-6.
- Ocelli, M.L. and Rennard, J.J.** (1988). Hydrotreating catalysts containing pillared clays. *Catalysis Today* 2; 309-319.
- Rana, M.S.; Samano, V.; Ancheyta, J.; Diaz, J.** (2007). A review of recent advances on process technologies for upgrading of heavy oils and residue. *Fuels*, 86, 1216-1231.
- Rodriguez, Y.M.V., Beltran, H.I., Vazquez-Labastida, E., Linares-Lopez, C., Salmon, M.** (2007). Synthesis and characterization of montmorillonite clays with modulable porosity induced with acids and superacids. *Journal of Materials Research* 22 (3), 788-800.
- Rosenquist, I.Th.** (1959). **Montmorillonitt fra Skyverdalen I Hemseedal.** *Norsk Geologisk Tidsskrift* 39, 350.
- Sakizci M., Alver B.E., Alver O. and Yorukogullari E.** (2010). Spectroscopic and thermal studies of bentonites from Ünye, Turkey. *Journal of Molecular Structure*, 969, 187-191.
- Shan, Z.F. and Guang, W.J.** (2001). Advances in Chemical Viscosity-Reducing Methods and Techniques for viscous Crude Oils. *Oilfield Chem*, 3, 24.
- Sabu, K.R., Sakumar, R., Rekha, R. and Lalithambika, M.,** (1999). A comparative study on  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HClO}_4$  treated metakaolinite of a natural kaolinite as Friedel-Crafts alkylation catalyst. *Catalysis Today* 49, 321-326.
- Salahudeen N., Ahmed A. S., Ajinomoh C S., Hamza H. and Ohikere A.** (2012). Studies on the Mineral and Chemical Characteristics of Pindiga Bentonitic Clay. *Petroleum Technology Development Journal*. 2. 55-62.
- Sanabria, N., Alvarez, A., Molina, R. and Moreno, S.,** (2008). Synthesis of pillared bentonite starting from the Al-Fe polymeric precursors in solid state, and its catalytic evaluation in the phenol oxidation reaction. *Catalysis Today* 133-135, 530-533.
- Schmidt C., Zhou M., Marriott H., Morgner N., Politis A. and Robinson C. V.** (2013). Comparative cross-linking and mass spectrometry of an intact F-type ATPase suggest a role for phosphorylation. *Nature Communication*, 4, 1-11
- Schoonheydt, R. A.** (2002). Smectite-type clay minerals as nanomaterials. *Clays and clay Minerals* 50 (4), 411-420.
- Swarnakar, R., Brandt, K.B. and Kydd, R.A.,** (1996). Catalytic activity of Ti- and Al- pillared montmorillonite and beidellite for cumene cracking and hydrocracking. *Applied Catalysis A: General* 142; 61-71.



- Shallsuku, P.** (2008). Structural characterization of Asphaltenes in Nigerian crude oil. Society of Petroleum Engineers (SPE) distinguished lecturer program.
- Speight J. G.** (1988). Asphaltenes and the structure of petroleum. In: Speight JG, editor. Petroleum chemistry and refining. Washington (DC): Taylor and Francis Publ.. p. 103.
- Speight, J. Petroleum Asphaltenes** (2004). Part 1 Asphaltenes, resins and the structure of petroleum. *Oil Gas Sci. Technol*, 59, 467-477.
- Speight, J. G.** (1998). *The Chemistry and Technology of Petroleum*. pp. 412–467. Marcel Dekker, Inc., New York, NY, USA.
- Thomas, J.M. and Thomas, W.J.,** (1997). Principles and Practice of Heterogeneous Catalysis. *VHC Publishers Inc.*, New York.
- Tran N.H., Dennis G.R., Milev A.S., Kamali Kannangara G.S., Wilson M.A. and Lamb R.N.** Interactions of sodium montmorillonite with poly(acrylic acid). *Journal of Colloid and Interface Science*, **2005**; 290, 392–396.
- Vaughan, D.E.W.,** (1988). Pillared clays - a historical perspective. *Catalysis Today* 2, 187-198.
- Veith, E. J.** (2007). Performance of a Heavy to Light Crude Oil Upgrading Process. In Proceedings of the International Oil Conference and Exhibition in Mexico, Veracruz, Mexico, 27-30 June.
- Zhou C. H. and Keeling J.** (2013). Fundamental and Applied Research on Clay Minerals: From Climate and Environment to Nanotechnology, *Applied Clay Science*, Vol. 74, 3-9.

