Development of semi-synthetic catalyst based on clay and their use in catalytic cracking of petroleum residue

Oumarou Abdoulaye Dan Makaou^{1,2} · Soumahoro Gueu¹ · Marou Gourouza³ · Kouassi Benjamin Yao¹

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Abstract

Two semi-synthetic clay-based catalysts were prepared. These catalysts were obtained by incorporating lanthanum oxide (Cat1) and chromium oxide (Cat2). They were then tested for catalytic cracking of a heavy petroleum residue (fuel). The two formulations were carried out in the presence of silica to improve their acidity then underwent an acid activation. The catalysts obtained were characterized by various methods (XRD, FTIR, ICP-OES, SEM). The results showed that the incorporation of oxides and the addition of silica improves the structural characteristics of the final products. The support used was a kaolinite rich clay, having a specific surface area of 15.26 m²/g and acidity of 14 meq/g. These values increase, respectively, to 456.14 m²/g and 50 meq/g for Cat1 and to 475.12 m²/g and 57 meq/g for Cat2. The influence of the type of oxide incorporated, the specific surface area, the porosity and the acidity of the catalysts on their catalytic activity was studied. The nature of the oxide used proved to be decisive on the quality of the catalyst. Thus Cat1, prepared with lanthanum oxide, showed the best performance in cracking the petroleum residue achieving a conversion rate of 74.13% compared to 66.53% for cat2.

Keywords Petroleum residue · Clay · Catalyst · Catalytic cracking

Introduction

Due to its impact on the environment, the use of heavy oil residue (fuel) is strongly discouraged by government officials. Thus, the demand of fuel will suffer a sharp drop in coming years in favor of gasoline, diesel and other petroleum products, which are lighter. To remain competitive and give added value to heavy oil residues, the refineries are stepping up their research to improve the fluid catalytic cracking (FCC) process [9, 19]. The FCC process consist to convert heavy oil feeds into light products. Although this process has been used in refineries for decades, it needs to

be innovate to achieve performance [2, 25]. Therefore, new catalyst development need to be investigated to improve the yield of FCC processes.

A catalyst is a substance that increases the rate of a chemical reaction, without being consumed or produced [8]. The activity and selectivity of the FCC catalyst are derived from the acidic sites and the pore structure, respectively. Catalytic catalysts are therefore porous solids with acidic properties [4, 18, 23]. Commercial FCC catalysts generally consist of two main components: the zeolite and the matrix. The zeolites used in FCC catalysts are mainly synthetic faujasite Y type zeolites and high silica Y zeolites, which are the main contributor to the catalytic activity and selectivity of the FCC catalyst [13]. The matrix is made of different constituents such as aluminosilicates and additives which are solid compounds added to improve its properties [4, 9]. Nevertheless, the high cost of these commercial catalysts could be a barrier to their use in development countries. It is urgent to develop a novel FCC catalyst with local resource [20, 26].

Recent research is directed towards the development of semi-synthetic clay-based catalysts. In this configuration, the clay acts as a matrix in which metallic oxides are incorporated. Emam [8] has shown that clay catalysts are arousing much interest for catalytic application in the

✉ Soumahoro Gueu
Soumahoro.gueu@inphb.ci

¹ Laboratoire des Procédés Industriels, de Synthèse, de L'Environnement et des Energies Nouvelles (LAPISEN), Institut National Polytechnique Félix Houphouët-Boigny, Yamoussoukro BP 1093 Yamoussoukro, Côte d'Ivoire

² Département Energies Fossiles, Université D'Agadez, BP 199 Agadez, Niger

³ Département de Chimie, Faculté Des Sciences Et Techniques, Université Abdou Moumouni de Niamey, BP 10662 Niamey, Niger

petroleum refining industry. According to Bouras [6], the interest given in recent years to the study of clays by laboratories around the world is explained by their abundance in nature, the importance of their specific surface, their porosity and especially their ability to exchange interfoliar cations. Kaolin and montmorillonite are the most commonly used clays in the development of refining catalysts [20]. Murray [21] estimates that more than 200,000 tonnes of kaolin are used annually to produce petroleum cracking catalysts. This work deals with the development of new semi-synthetic catalysts based on clay and oxides, the characterization of these catalysts obtained and finally their use in fuel cracking. To our knowledge, in the literature, it has not been reported cracking of fuel oil by semi-synthetic catalysts or even by conventional catalytic catalysts. This study therefore aims to fill this void.

The objective of the current work was to prepare a FCC catalyst, and to study the catalytic properties. Two catalysts were prepared using a kaolinite rich clay as matrix. The influence of the type of oxide incorporated, the specific surface area, the porosity and the acidity of the catalysts on their catalytic activity was studied.

Materials and methods

Materials

The catalysts prepared in this study were made from Niger clay. This clay has been characterized in previous work [1]. It has a specific surface area of 15.26 m²/g and a loss on ignition of 16.1%. It is mainly composed of kaolinite (46.3%) and an interstratified smectite illite chlorite (53.7%) [1]. The choice of this clay is explained because the catalytic reactions taking place at high temperature (≥ 500 °C), the catalyst must be a refractory material, able to withstand such temperature.

Catalyst preparation

In a beaker containing 15 g of clay with a particle size less than 2 μm , 0.55 g of lanthanum (La₂O₃) or chromium (Cr₂O₃) oxide and 4 g of silica are added. After homogenization, acid activation is carried out by adding 25 mL of 10% hydrochloric acid and then the whole is left under stirring for 6 hours. The resulting mixture is dried at 105 °C for 12 hours and then calcined at 800 °C for thirty minutes. The catalyst containing lanthanum oxide is called Cat1 and the one obtained with chromium oxide is called Cat2.

Catalyst characterization

X-ray diffraction (XRD) patterns of all samples were recorded at room temperature, using a Rigaku-Miniflex II diffractometer (Japan). The incident radiation is generated by the K α line of copper ($\lambda = 1.5406$ Å) at 30 kV and 15 mA. The analyzes were carried out in the angular interval [5–70°] in 2 θ with a step of 0.02° (2 θ) and a counting time of 2 s.

The infrared spectroscopic analyzes were carried out in ATR (Attenuated Total Reflectance) mode with a Fourier Bruker Alpha Transform spectrometer equipped with a diamond crystal (refractive index of the diamond 2.451). The spectra were acquired with a nominal resolution of 4 cm⁻¹ over a wavenumber range from 400 to 4000 cm⁻¹.

Chemical analysis of the samples was performed using a Vista Pro Varian instrument equipped with an ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) plasma.

The BET isotherms were obtained using a Nova Station B sorptiometer. The absorption gas used is nitrogen and the measurements are carried out at 77.350 K. The determination of the microporous volumes and the microporous surfaces are carried out by the t-plot method.

A variable pressure scanning electron microscope (SEM) from the D.C.A.R. (SEM FEG Supra 40 VP Zeiss) of 2 nm resolution coupled to an X-ray microanalyzer (EDS) was used for the characterization of the microstructure and the surface chemical composition of the catalysts.

The total acidity of the catalysts was determined using the titration method of Boehm [5] which is used by many researchers working on adsorbents [12]. This method consists of assaying functional groups having various acidities with different bases. For the present study, the bases used are sodium hydroxide (NaOH), sodium hydrogen carbonate (NaHCO₃) and sodium ethanolate (C₂H₅ONa). The procedure is as follows: a mass of 500 mg of catalyst is placed in Erlenmeyer flasks. Then 25 mL of the different bases, all prepared at 0.1 N, are transferred into each of the Erlenmeyer flasks containing the catalysts. The blank tests are carried out by proceeding in the same manner, with the difference that Erlenmeyer flasks do not contain a catalyst. The samples and the blanks are stirred on magnetic stirrers at 150 rpm for 72 hours at room temperature, then left to stand for 6 hours. The supernatant is filtered through a Whatman cellulose nitrate membrane (0.2 μm) then the excess basic solution is dosed back with a 0.1 N HCl solution.

Catalytic cracking test

The performance tests of the catalysts were carried out in a stainless steel reactor (Fig. 1), manufactured in the

Fig. 1 Model of the cracking plant

laboratory (LAPISEN). The methodology used here has been adapted to that of Houdry [14]. To carry out the cracking operation, a mass of 20 g of catalyst is placed in a reactor. Then, the reactor is inserted into an electric furnace and the temperature is raised in steps of 100 °C until reaching 500 °C. After checking the seal of the installation, a mass of 50 g of pre-heated petroleum residue is injected into the reactor. The reactor temperature is constantly checked by a probe thermometer (TYPE K/J) and maintained at 500 °C. The cracked products leave the reactor by passing through a refrigerating condenser and are recovered in the form of droplets in recipe flasks. The cracking operation is stopped when there is no more droplet drop in the receiving bottle.

The yield (Eq. 1) was calculated from the ratio between the mass of the product obtained after cracking (m_o) and the initial mass introduced into the reactor (m_i).

$$x_i = \frac{m_o}{m_i} * 100 \quad (1)$$

Results and discussion

XRD

The two catalysts developed (Cat1 and Cat2) were analyzed by the XRD method. The results obtained are given in Fig. 2. The XRD pattern of the clay (support) shows various clay minerals. The presence of smectite and illite is indicated by the peaks located at 6° and 9° respectively. The intense peaks at 12.5° and 25° are relative to kaolinite and the peak appearing around 26.78° is characteristic of quartz. It can also be seen that the XRD pattern of clay exhibited the crystalline features. The XRD patterns of the catalysts show the disappearance of all kaolinite peaks initially present in clay. Indeed, from 580 °C, kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) loses the hydroxyl OH function and it is transformed into metakaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). This is confirmed by the XRD patterns of the catalysts that show a characteristic appearance of an amorphous material. The presence of metakaolinite, a refractory material, in these catalysts is an advantage for their use as cracking catalysts.

Moreover, the presence of La_2SiO_5 is identified at 27.84° (2θ) [7] and 34.9° (2θ) on the Cat1 spectrum [29]. This oxide (La_2SiO_5) results from the reaction between lanthanum oxide and silica, as predicted by Sun [29], in the following reaction (Eq. 2):

Fig. 2 XRD pattern of clay (support) and catalysts

(2)

The characteristic phases of chromium oxide (Cr_2O_3) have been identified on this spectrum. They correspond to the peaks at 54.14° ; and 64.04° (2θ) according to Karimi [17].

FTIR spectroscopy

The Fig. 3 shows the IR spectra of the clay (support) and the two catalysts produced. The spectrum of the support is characteristic of a clay. It shows the deformation vibration modes of structural hydroxyl groups between 950 and

Fig. 3 IR spectra a support, b Cat1, c Cat2

800 cm^{-1} . The absorption bands observed at wavenumbers 1034, 1100 cm^{-1} and 1159 cm^{-1} are characteristic of the antisymmetric modes of elongation of Si–O and Al–O bonds in aluminosilicates [10]. A comparative analysis of the spectrum of the support and those of the catalysts shows a remarkable change in structure. The difference observed could be related on the one hand to the new elements that were added in the preparation and on the other hand to the calcination that the catalysts underwent. The absorption band at 500 cm^{-1} is attributed to the vibration mode of the La–O bond of lanthanum oxide according to Saravani and Khajehali [28]. This peak confirms the presence of La_2O_3 phase in the Cat1 sample. The bands observed around 581 and 647 cm^{-1} are characteristic absorption bands of Cr_2O_3 on the Cat2 spectrum according to Nguyen et al. [22].

Catalyst acidity

The acidity of the catalysts measured by Boehm method indicates higher values of acidity for the catalysts compared to that of the support. Initially equal to 14 meq/g for the support, the acidity was evaluated at 50 meq/g for Cat 1 and 57 meq/g for Cat2. This significant increase could be justified by the presence of oxides which were added during processing. These acidity values are lightly superiors to those of the FCC zeolite catalysts (30–50 meq/g) used by Ibarra et al. [16]. This suggests that the catalysts developed here would be efficient in cracking test as industrial catalysts from the point of view of surface acidity.

Chemical analysis

The chemical analysis of catalysts are given in Table 1. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the support was equal to 2.08, similar to that obtained by Gueu et al. [11]. The SiO_2 content in Cat1 and Cat2 catalysts are 59.1% and 61.9% respectively. This content was initially equal to 49% in the support. The observed increase is due to the addition of silica during the preparation of the catalysts. According to Otmani [24], silica give good mechanical strength to catalysts and increase their acidic character [18] for the catalytic cracking operation. Furthermore, the SiO_2 contents of the catalysts are higher than that of the commercial FCC catalyst (54.1%) used by

Hussain et al. [15] for the catalytic cracking of vacuum gas oil.

Textural analysis

Specific surface

The specific surfaces of the catalysts produced were evaluated by the method of Brunauer, Emmet and Teller (B. E. T). They are 456.14 m^2/g and 475.12 m^2/g for the Cat1 and Cat2 respectively. The results obtained show that the surfaces have increased considerably compared to the specific surface of the clay support (15.26 m^2/g). This is due to the acid activation performed during formulation. This considerable increase is also observed in the literature [3, 13] and reflects a significant development of microporosity. The values obtained in this study are better than 347 m^2/g and 177 m^2/g , representing the surface areas calculated by He et al. [13] and Al-Khattaf [3] respectively. In addition, Ribeiro et al. [27] found specific surface areas of 266, 276 and 422 m^2/g for commercial FCC catalysts which are also lower than those of the catalysts developed here. These results once again show the good characteristics developed by the catalysts prepared in this work.

Porosity

The porosity of the catalyst is a very important factor. It is established that the diffusion of molecules from the residue to be cracked is easy when the dimensions of the pore are 2–6 times larger than those of the molecules [30]. The data (Table 2) show that the diameters and the pore volumes increased considerably after the preparation of the catalysts. The type of oxide used does not influence the pore diameter which remained similar for

Table 2 Pore diameters and volumes of prepared catalysts

Catalysts	Average pore diameter (nm)	Pore volume (cm^3/g)
Support	0.75	0.18
Cat1	2.12	0.49
Cat2	2.15	0.24

Table 1 Chemical analysis of catalysts

	Chemical composition (%)											
	SiO_2	Al_2O_3	Fe_2O_3	MgO	TiO_2	CaO	Na_2O	K_2O	P_2O_5	La	Cr	LOI ^a
Sup-port	49	23.5	4.1	2.19	1.35	1.76	0.45	0.93	0.3	–	–	16.1
Cat1	59.1	19.1	3.31	1.44	1.18	0.5	1.21	0.63	0.25	2.5	0.01	7.5
Cat2	61.9	19.4	4.52	1.76	1.13	2.05	0.37	0.77	0.24	0.01	0.01	5.3

^aLoss on ignition

the two catalysts. The pore volume developed by Cat1 is significantly greater than that of Cat2.

SEM

The images obtained by scanning electron microscopy (SEM) and X-ray microanalysis of the catalysts are presented in Figs. 4 and 5.

Fig. 4 SEM image and X-ray microanalysis of Cat1

Fig. 5 SEM image and X-ray microanalysis of Cat2

Figures 4 and 5 show that the catalysts mostly consist of very fine particle clusters. These images show a certain homogeneity in the composition of the samples. However, the Fig. 4 shows clusters in the form of aggregates. This particularity could be justified by an incomplete grinding of the Cat1 sample during its SEM preparation. In addition, grains of quartz (SiO_2) are also observed on these images. This confirms the above analyses.

The results of the X-ray microanalysis of the catalysts indicate the presence of several elements such as silicon (Si) which is the most abundant element in all samples. It's to be note the appearance of lanthanum (La) in Fig. 4 and the appearance of the element chromium (Cr) in Fig. 5. The presence of these elements (La and Cr) confirms the incorporation of the oxides.

Catalytic cracking yield

The catalysts developed here were used in the cracking of a petroleum residue. The cracking tests take place at 500 °C with a ratio fuel/catalyst (g/g) equal to 4.5. The results recorded show a conversion rate of 74.13 and 66.53% for the Cat1 and Cat2 respectively. The acidity of the catalysts is very often considered to be the most important parameter. The greater the activity, the greater the catalytic efficiency. This assertion is not verified in this study. Indeed, despite its low acidity, Cat1 has the best yield. This would be attribute to its specific surface area and its pore volume which are high than those measured for Cat2.

Conclusion

The objective of this work was to develop clay-based catalysts to crack a heavy oil residue. XRD and infrared analyzes of the prepared catalysts confirmed the presence of lanthanum oxide and chromium oxide. This indicates that the oxides have been well incorporated showing at the same time that the method of preparation is suitable. Textural analysis showed that the incorporation of oxide, acid activation and calcination carried out during processing strongly influenced the composition and textural properties of the catalysts. The specific surfaces increase from 15.26 m^2/g for the support to 456.14 and 475.12 m^2/g for the Cat1 and Cat2 respectively. Pore volumes also increased from 0.18 cm^3/g for the support to 0.49 cm^3/g and 0.24 cm^3/g for Cat1 and Cat2 respectively. Compared to the support, the acidities of the two catalysts are very higher. This was related to the addition of silica and acidic activation made during catalysts preparation. Finally, the catalytic cracking results indicated a conversion rate of 74.13 and 66.53% for Cat1 and Cat2 respectively. From this study, the use of this clay for the

development of semi-synthetic catalysts would be particularly interesting to the refining industry.

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