Synergetic effects of hierarchical porosity, chemical, acidic, and hydrothermal modification of the NaY zeolite and their simultaneous use in the technology of the Fluid Catalytic Cracking (FCC)

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ABSTRACT: *Currently, fluid catalytic cracking (FCC) is one of the largest and most important conversion technologies in the oil refinery industry. In this regard, cracking activity and selectivity are influenced by some factors like acid activation, surface area, and pore structure of ultra-stable Y zeolites (USY). To achieve this goal, different chemical and hydrothermal treatments of zeolite were investigated to stabilize the catalyst and increase the conversion for the process of catalytic cracking. This work focused on the properties and expected behavior of two types of modified Y zeolite both of which are based on NaY zeolite. To improve the stability of zeolites and the selectivity of the catalyst, they were treated with different techniques such as chemical (adding rare earth elements (REE) or boric acid), acidic (hexafluorosilicic acid), and hydrothermal techniques. Finally, they were used simultaneously in the formulation of the FCC to improve its performance which is undoubtedly have a tremendous impact on FCC products as a major process in conversion. The characterization of the modified zeolites and the final product of the FCC catalyst were performed by X-ray fluorescence spectrometry (XRF), X-ray diffraction spectrometry (XRD), N_2-porosimetry, inductively coupled plasma - optical emission spectrometry (ICP-OES), scanning electron microscopy (SEM), and Temperature programmed desorption (TPD). Accordingly, XRF showed a high silicate content level in synthesized zeolites, XRD indicates the appropriate Si/Al ratio value in the final product, N_2-porosimetry revealed the formation of porous zeolite crystal in their sodalite cage, and the presence of micro-meso structure of USY samples with higher microporosity. ICP-OES was used to determine the percentage of boron. The obtained FCC catalyst was evaluated in a micro-activity testing (MAT) unit, also Carbon-Hydrogen-Nitrogen analysis (CHN), Thermo gravimetric analysis (TGA) were done to measure the coke content of spent FCC to prove the better performance of the FCC catalyst.*

INTRODUCTION

One of the most important catalytic conversion units and processes in the world, which converts heavy and low-value petroleum materials into lighter and more valuable materials, is the catalytic cracking process, which is a major source of propylene production. Today, due to the increase in fuel consumption in the world and the need to convert heavy materials into light fuel materials, the need for this process is felt more and more [1]. Considering that the FCC process has been used commercially for about a century, nevertheless, the catalyst production of this process and its improvement is still being studied in many academic and industrial centers of the world [2]. During this century, the entry of zeolites, as a solid acid catalyst, into the petroleum refining industry has attracted enormous attention as the main component of the FCC catalyst [3-4]. In fact, FCC is multi-component material whose main and active matrix is faujasite or zeolite Y, and materials such as alumina, binding system, silica sol, and inert matrix like clay are the other components. This material provides a sustainable route for industrial applications and is offered to upgrade large molecules such as heavy oil and biomass, maximize the gasoline yield of refineries, and used to convert gas oil into gasoline-range hydrocarbons [5].

Y zeolites are porous structures with acidic sites that can convert larger molecules into molecules in the gasoline range. Clay is used as a filler to increase the heat capacity of the catalyst in these catalysts. Various sources of alumina and silica are used to produce a matrix with meso and macro pores that allow the entry of larger feed molecules for the breaking process. Other additives can also be used as metal traps to trap nickel and vanadium metals in food [6-7]. As mentioned above, Type Y zeolites are the major active centers for large molecules to transform heavy oil fractions into transportation fuels and petrochemical feedstocks [8]. But like other cracking processes, over time the catalytic activities of these composites decrease due to the deactivation of Y type zeolite caused by the formation of coke and cover the active sites. The activity term represents the relative ability of the catalyst to convert heavy petroleum hydrocarbons into light and valuable hydrocarbons under certain conditions of temperature, pressure and time. This problem is compensated by adding new catalyst to the system. So, there is a constant interest to prolong their lifetime and improve their performance. To overcome these problems, the impact of hierarchical zeolites cannot be ignored in reactions involving large molecules by coupling the native micropores with an intra-crystalline mesopores network [9-10]. On the other hand, their significant increase in gasoline efficiency and more efficient utilization of the petroleum feedstocks in refinery operations is important due to having a direct impact on the global economy [8]. Hence, the FCC catalyst compositions are modified by tuning their formulation and different types of zeolite and other additives to enhance the yield of this process [11-12]. Among the modified zeolites, the USY zeolites are widely used in the FCC process due to their catalytic performances which are gravely affected by metal contaminants present in crude oil and their microporous crystalline silica-alumina frameworks, acid site, and very large surface areas [13-14]. On the other hand, there are some common ways to stabilize the zeolite structure like dealumination to improve the Si/Al ratio of zeolite which often led to confined mesopores. In other words, the combination of dealumination techniques such as acid treatment and steam with other chemical techniques are necessary to generate mesopores in the zeolite with a low Si/Al ratio [10]. In fact, use of these techniques, in the formulation of FCC catalyst, provide a new worldwide performance for the global supply of fuels and chemicals [15-16]. As a result, extensive studies have been conducted to develop and modify zeolite Y in FCC catalysts to improve coke selectivity, higher cracking activity, and greater stability [17-18]. Indeed, as mentioned previously, the performance of the FCC catalyst is measured by various parameters like conversion rate, selectivity, efficiency, activity and carbon content on the

catalyst which all these parameters are dependent on the modification of Y zeolite. Therefore, the continuous changes in the demanded products along with the changes created in the oil feed have caused a continuous change in this process. Moreover, stabilizing the agent and promoting the active protonic sites via ion exchange, and introducing mesopores, REE, and other elements in the zeolites component, have been becoming them an effective material compared to the inherent microporous nature of zeolites [19-20]. In fact, the small radius of REE cations is more favorable for H_2O contact with framework atoms. So, Al-O bonds with relatively weak energy are broken and replaced by Si-O bonds. As a result, shorter Si-O bonds make the unit cell smaller. Instead, increasing the radius of REE ions increases the hydrolysis reaction and increases the number of OH groups attached to RE ions, and avoids the dehydration reaction between Si-OH-Al groups during calcination, and the size of the unit cell decreases with the decrease of RE ion radius. As mentioned above, the activity and stability of type Y zeolites can be modified by some treatments to avoid negative effects such as partial clogging of the frame work during steam [21-23]. In particular, determining the crystal size of the Y type zeolites is very important which are the active phase of FCC catalysts and can affect gasoline composition and some critical parameters such as micro-meso pore size, size distribution, and Si/Al ratio to maintain the chemical and physical properties of the zeolites [24-26]. Consequently, studies about type Y zeolites containing Si, Al (which are tetrahedrally coordinated), and other elements have received *considerable attention* due to their unique properties [27-28]. Literally, to enhance activity and structural resistance and impact on unit cell size stabilization, commercial elements, and other treatment techniques are usually used separately in the modification of zeolites [28-29]. So, these issues highlight the need to improve the thermal stability, acid properties, activity, and selectivity of cracking catalysts.

In this work, various chemical, acidic and hydrothermal techniques enabled us to develop hierarchical porosity and high acidities as essential aspects for the effective catalytic properties of NaY zeolite to turn them into ultra-stable zeolites and simultaneous use in FCC catalysts. For this purpose, two types of zeolite Y with different modifications were synthesized both of which were prepared from NaY. In one of them, the rare earth elements were used as chemical modifiers. In fact, our main aim of introducing rare earth compounds in the NaY zeolite is not only to affect the cracking activity but it is also to have consequences for the hydrogen transfer properties of the catalysts. On the other hand, chemical modification of another zeolite was done with boron precursor which can change the acidic and shape-selective properties of the based zeolite by destroying the structure of the Y zeolite and thus decreasing the total acid sites and strong acid sites of the Y zeolite. Besides, acid treatment was carried out by H_2SiF_6 in this zeolite. Finally, steam treatment and calcination were used for both of the synthesized zeolites, which caused the adjustment of acidic and textural properties. By this combination of methods, the acidity, selectivity, and performance of the FCC catalysts that contain both of these synthesized zeolites simultaneously are higher than that of FCC catalysts, which have one type of zeolite modified by different techniques [23]. All of these results were obtained by three main techniques e.g., XRD which was used to determine the crystal and the zeolite structure, XRF spectrometry to indicate the elemental analysis and Si/Al ratio, and BET analysis to measure the specific surface area and total pore volume. Additionally, to verify the results and obtain further investigations, some other techniques such as ICP-OES, SEM, TGA, CHN, MAT, and TPD have been used for zeolites and FCC catalysts.

EXPERIMENTAL SECTION

Materials

NH$_4$Cl, La(III) Chloride, Cerium (III) Nitrate, hexafluorosilicic acid (H$_2$SiF$_6$), and boric acid (H$_3$BO$_3$) used for USY zeolites were purchased from Merck Chemical Co. (Darmstadt, Germany). Sodium silicate, aluminum sulfate, pseudoboehmite alumina, kaolin clay, and *Citric* acid were applied in the formulation of FCC, and the other reagents were of analytical grade and bought from Merck chemical Co. (Darmstadt, Germany).

Sample preparation

This study was carried out with two types of Y zeolite, both of which were based on NaY zeolite. The base NaY zeolite was synthesized as mentioned in some literature [18].

Firstly, the sample NaY slurry with a liquid-to-zeolite ratio of 5:1 was subject to NH$_4^+$ ion exchange in 200 g L^{-1} NH$_4$Cl solution and 60 g L^{-1} H$_3$BO$_3$. In the second step after washing with deionized water, adjust pH at 3 using hydrochloric acid solution, filtered, dried at 105 °C, calcined in a muffle furnace at 600 °C for 2h, and steamed at 800 °C for 3h, the sample was further ion-exchanged in 120 g L^{-1} H$_2$SiF$_6$ and 200 g L^{-1} NH$_4$Cl solution, followed by the dealumination process. The final slurry was washed with deionized water and dried in the oven (105 °C) to obtain first zeolite which named USY 1 with a unit cell size (UCS) of 24.51 A°.

The second zeolite named USY 2 with a UCS of 24.52 A° is also obtained from the NaY zeolite. In the first step, La(III) Chloride (220 g L^{-1}), Cerium (III) Nitrate (90 g L^{-1}), and NH$_4$Cl (200 g L^{-1}) were added with a liquid-to-zeolite ratio of 3:1. In the next step, after washing with deionized water, adjust pH at 3 using hydrochloric acid solution, filtered, dried at 105 °C, calcined in a muffle furnace at 600 °C for 2h, and steamed at 800 °C for 3h, ion exchange was done once more by NH$_4$Cl (200 g L^{-1}) and then washed, filtered, dried like USY 1.

Both synthesized zeolites were applied simultaneously in the formulation of the FCC catalyst in which the ratio of USY 1 to USY 2 is 1 to 3. Then, specific filler and binder were added based on the U.S. Pat. No. 4,142,995, and sodium silicate as silica source, aluminum sulfate, kaolin clay, and *Citric* acid were added in each step according to the instructions. Place the mentioned slurry in the spray drying stage to obtain spherical particles and then place the particles in a calcination stage.

Instrumentatio

The multi-elemental analysis of samples was carried out using a wavelength dispersive X-ray Fluorescence (WD-XRF) spectrometer, Thermo Scientific™ ARL™ OPTIM'X model (Cu X-ray tube; 50keV maximum power), equipped with an automatic sampler for 13 pellets. Due to the limitation of WD-XRF crystals, ICP-OES (Spectro Genesis Fee, Germany) was used to determine the boron element percentage in USY 1. To determine the crystallographic structure and UCS of the materials, XRD spectrometer (Rigaku, MiniFlex, 600 W X-ray tube) was used. Identification of specific surface areas and pore size distributions was measured by BET analysis (BELSORP-MAX-G) which allows measuring adsorption isotherms in a wide range. The morphological characterization of samples was carried out using a scanning electron microscope (SEM) (Cambridge S360). The representation of sample size was obtained to use and ideally, the sample's shape, state, and microscope's detection capacity were considered. Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer Pyris Diamond TG/DTA, with a heating rate of 20 °C/min under N$_2$ atmosphere to determine the thermal stability of the samples. Also, it was performed to characterize the activity and deactivation behavior of spent FCC and

provide a relationship between catalyst activity and coke content. Due to using multiple analytical techniques for the determination of coke composition and structure, CHN device (TruSpec, LECO, USA) is used to determine coke amount in FCC catalyst by elemental measurement of carbon, hydrogen, and nitrogen in the FCC sample. TPD (micromeritics, 2900-TPD/TPR) of basic molecules from the surface of samples has been used to measure their acid properties and surface catalysis study. The TPD experiment consists of sorbing a base molecule on the material of interest and flushing the surface with an inert gas to measure the desorption of the base. By quantitatively measuring the amount of base desorbed and noting the temperature(s) of desorption, information can be obtained on both the intrinsic and extrinsic acid properties in a single experiment. The evaluation of FCC catalysts is typically performed using a micro activity test (MAT) (MAT Micro reaction Test Unit for FCC, China). Although many tests exist to evaluate the acidity of a catalyst, a property is important in FCC catalysis, the ultimate test consists of determining the activity and selectivity of the catalyst using a standard feed under close to commercial operating conditions.

RESULTS and DISCUSSION

A great deal of attention has been paid to modifying the Y type zeolites in FCC catalysts which not only can improve the density and strength of acid sites in the pores of zeolite Y, but also can direct more hydrocarbons to enter into the pores to convert crude oil into a more valuable product through a surface cracking reaction. In this study, NaY zeolite modifications were done through chemical modification (rare earth and boron), hydrothermal modification (steam), and acid modification (H_2SiF_6) for use in FCC catalysts simultaneously. The presence of REE enhance catalyst activity and prevent the loss of acid sites. Additionally, low content of H_3BO_3 as a mild inorganic acid in the zeolite structure will play an important role in cleaning micropores. However, higher H_3BO_3 amount inhibited the migration of aluminum species or combined with aluminium species to form new boron-oxygen-alumina species, giving rise to lower surface area and pore volume [29]. Besides, the dealumination with acid treatment by H_2SiF_6 and steam treatment were found to be useful for producing micro-meso structure zeolites. Priory, the characterization of these zeolites and FCC catalyst were performed using the most applicable instruments of XRF, XRD, ICP-OES, BET, FT-IR, TGA, CHN, SEM, TPD, and MAT.

Characterization of physical and chemical analysis of catalysts
XRF and ICP-OES analysis:

The chemical composition of the USY catalyst samples was determined by WD-XRF and ICP-OES spectrometer for determination of boron. As can be seen in Table 1, the chemical composition of the prepared USY catalysts including the contents of La_2O_3, Ce_2O_3 (both of them reported as RE_2O_3), Al_2O_3, SiO_2, B, and Na_2O. The test results listed in Table 1 have revealed the Si/Al ratio of 5-8 and 1-3 in zeolite Y and FCC catalyst from their chemical composition, respectively. Zeolite Y with high Si/Al ratio plays a key role in fluidized catalytic cracking process. The Si/Al ratio of zeolite Y determines the acidity, thermal and hydrothermal stability, thus affecting its catalytic activity. Highly siliceous zeolites are overwhelmingly had higher hydrothermal stability, higher selectivity to organic compounds, and often better catalytic properties in comparison with Al-rich zeolites. It is clear that due to the determination of extra-framework aluminum in XRF, the Si/Al ratio will be higher in XRD spectrometry, where extra-framework aluminum is not observed in it. In order to investigate the

changes in the acidity feature and catalytic performance the high silica Y zeolites were chosen as most suitable offering high stability in steaming conditions [24].

Table 1. Chemical composition of the prepared USY and FCC catalysts by XRF spectrometer.

Sample Item	USY 1	USY 2	FCC	Industrial index
Al_2O_3	17.10	20.63	51.69	≥45
SiO_2	80.45	66.24	43.9	-
Na_2O	0.66	0.73	0.17	≤ 0.3
RE_2O_3	-	11.2	3.1	3±0.5
B	0.7	-	0.3	-
Si/Al	8.33	5.68	1.44	1-3

XRD analysis:

As mentioned previously, high crystallinity is important to prepare high siliceous zeolite Y. To study the effect of dealumination on crystalline structure, internal structure examination, and patterns generation, the XRD patterns of the NaY, both USY zeolites and final FCC product were shown in Fig. 1.
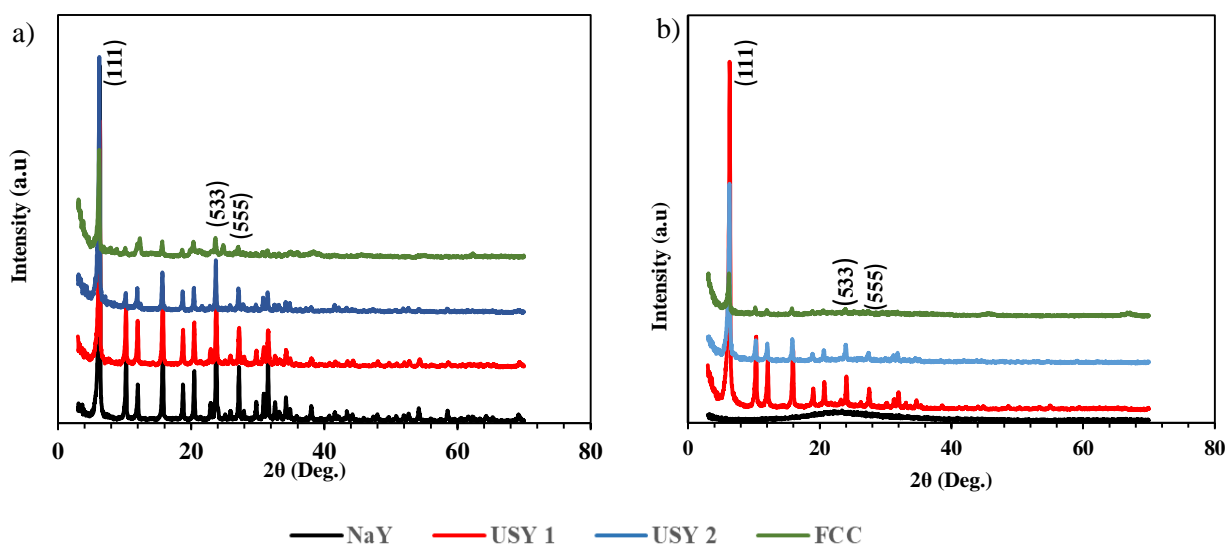
Fig 1. The XRD pattern of NaY, both USY zeolites, and final FCC product (a) before and (b) after 4 hours of reaction.

As can be seen in Fig. 1a, the XRD pattern of zeolite which is obtained before dealumination is exhibited NaY zeolite pattern with typical diffraction peaks 6.3, 23.5, and 31.2 which represents the maximum three peaks with the value of (111), (533), and (555) as hkl, respectively. The crystallinity, UCS, and Si/Al ratio of this sample were

89.3, 24.63, and 8.75, respectively which were calculated from this reference [25] that maximum crystallinity was observed compared with others. The XRD pattern of the dealuminated and modified USY 1 was showed that diffraction peaks remained stable without any shifting in a degree of the XRD pattern of NaY zeolite obtained before dealumination which exhibited the typical diffraction peaks at 6.3, 23.5, and 31.2 with the crystallinity, UCS, and Si/Al ratio of 73.6, 24.50, and 8.41, respectively.

The XRD pattern of the dealuminated and modified USY 2 was indicated that diffraction peaks remained stable without shifting in a degree of 2θ and the crystallinity, UCS, and Si/Al ratio were 48.7, 24.52, and 6.54, respectively, while peaks intensities decreased resulted from dealumination in both USY zeolites. Finally, in the case of the FCC sample, all peaks were decreased and many crystalline peaks were observed for the XRD pattern of the FCC crystal structure. The crystallinity and UCS were obtained 16.48 and 24.64, respectively. But, due to the presence of aluminum used in the structure of the binder, the calculation of the Si/Al ratio was not performed, but due to the increase in the amount of UCS, it can be understood that USY zeolites are suitable materials for the performance of the FCC catalyst. As mentioned above, the Si/Al ratio in XRD is higher than XRF, due to non-measurement of non-structural aluminum in USY zeolites by XRD. In fact, the acid density and the acid strength decreased with the increasing Si/Al ratio and it is known to influence the acid properties of zeolites. On the other hand, as can be seen in Fig. 1b, the effect of aging on the steam stability of zeolites samples and FCC catalyst was investigated. For this purpose, samples were steamed at 800 °C for 4 h. The XRD results clearly indicate that USY 1 and USY 2 retain a well-ordered structure upon steaming at 800 °C and their crystallinity were obtained 37.7 and 23.9, respectively. While NaY zeolite is almost totally destroyed by steaming and its crystallinity reaches zero. These observations indicate that USY 1 and USY 2 used in the FCC structure have high stability and their structures will not be destroyed during the FCC production process. Further investigations showed that even the FCC catalyst has high stability and in addition to preserving the ordered structure, its crystallinity reaches from 17 to 10.3 after 4 hours of steaming at 800 °C.

N₂-porosimetry Analysis:

Textural characterization of USY zeolites is one of the most important parameters for optimizing their applications in FCC catalyst. Literally, total surface area and porosity properties are two influencing factors for catalyst's performance since they determine accessibility of active sites and often relate to catalyst's activity. On the other hand, the pore structures including pore size distribution and pore volume, control transport phenomena and regulate selectivity in catalytic reactions. Quantitative estimates of micro-meso pore volume, surface area, and pore size distribution of zeolites and final product were obtained based on Barrett-Joyner Halenda (BJH), Brunauer-Emmett-Teller (BET). The effect of USY incorporation on the textural structural properties of the FCC catalyst was investigated by analyzing the data from N_2 adsorption/desorption isotherms. Nitrogen adsorption/desorption isotherms were obtained in the region of 0.001–0.995 P/Po. Fig. 2a, indicates the type (I) isotherm for NaY zeolite which is containing pores typical of solids having exclusively micropore size with a very small amount of mesopores. The isotherms of USY 1, USY 2, and FCC catalysts are type (V) and show the bimodal distribution of pores (micro-meso structured), which were obtained in Fig. 2a, respectively. Fig. 2b, presents the pore diameter for NaY, USY 1, USY 2, and FCC catalyst. The influence of the dealumintion steaming process on the inner pore system of the Y-type zeolite is proven with the measurements given in table 2.
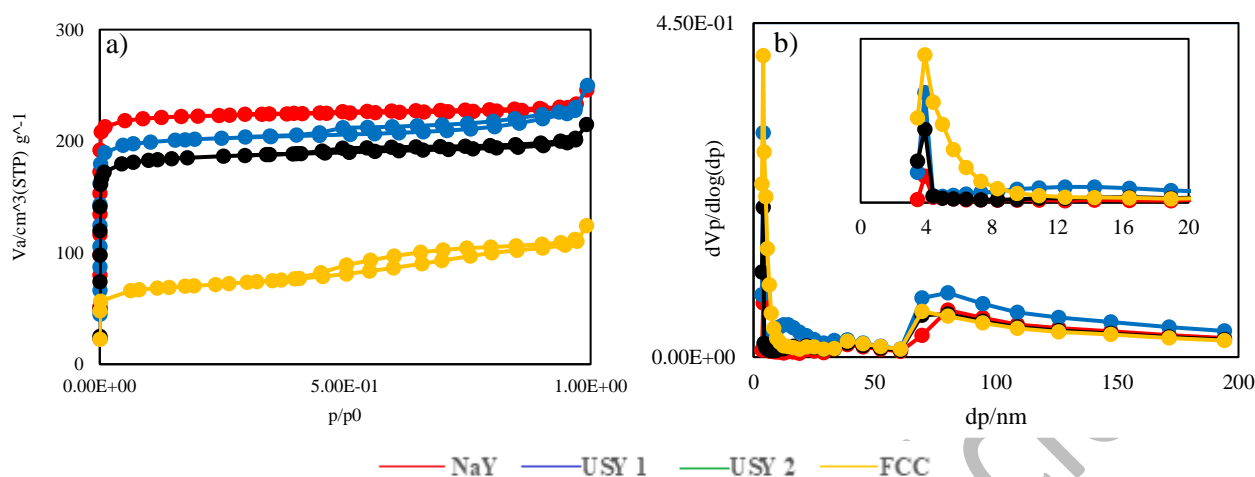
Fig 2. a) The adsorption/desorption isotherm and b) The BJH (micropore diameter) of NaY, USY 1, USY 2, and FCC catalyst

Table 2. BET surface, pore volume (p/p0 = 0.99), and micropore volume (t-Plot) in NaY, USY 1, USY 2, FCC.

Item \ Sample name	NaY	USY 1	USY 2	FCC	Unit
BET Surface	853.32	821.42	753.12	268.99	m^2g^{-1}
Pore Volume (p/p₀ 0.99)	0.3721	0.3824	0.3381	0.2019	cm^3/g
Pore diameter (BJH)	3.8	4	3.9	3.9	nm
Micropore volume(t-Plot)	842.195	787.689	722.209	193.279	cm^3/g

For better overview and understanding the results, in Table 1 and 2 the chemical composition and adsorption capacity of the samples are presented. As can be seen, at higher Si/Al ratios, the influence on the BET surface is quite strong. Although it depends on the operating temperature and healing time that is given during the synthesis. Therefore, the results indicate that not only the amount of surface area and N_2 adsorption has increased, but also the values of BJH and pore volume have increased. Additionally, increasing the Si/Al ratio in both USY samples provides the optimized synthesis condition process for the FCC catalyst which has high performance due to the high conversion and gasoline yield. Actually, USY zeolites exhibited high cracking. To identify the most effective catalyst for cracking, the effect of the Si/Al ratio of the USY zeolite on the catalytic activity and product yield was investigated in the following sections. Moreover, the hierarchical structure of zeolites affects the catalytic stability of the FCC catalyst. Accordingly, these zeolites exhibited high and stable activity with low coke formation compared with the macro-sized zeolite.

Temperature-programmed desorption (TPD):

The acidity properties of the Y zeolite samples and FCC catalyst were determined using the NH_3-TPD method, which was performed using an ordinary flow-type apparatus with a closed circulation system for gas adsorption and a thermo-conductivity cell in a He flow for the determination of desorbed gas. RRE and boron were used in the structure of zeolites due to their oxidation state nature to examine their effect on catalytic acidity. We expect

that these elements can add valuable properties to the zeolites and induce zeolite acidity. As shown in Fig. 3, the TPD profile of Y zeolite samples and FCC catalyst showed two peaks, in which for USY 1 and USY 2 the peak around 120 °C is assigned to the desorption of NH_3 from weak acid sites and the peak around 250 °C is ascribed to the desorption from strong acid sites. But, as can be seen in the TPD profile of USY 1, it is a stronger acid than USY 2. Moreover, the only TPD peak of NaY is around 100 °C and for FCC catalyst, the TPD profile showed two peaks around 100 and 450 °C. The peak position is a measure of the strength of acid site that peak position transition to the lower temperature is a measure of decreased acidity strength. Whereas the amount of acid site is calculated from desorption peak areas [26]. Therefore, based on Fig. 3, the strength of acid sites increased with the following order: NaY, USY 2, USY 1. As a conclusion, USY 1 and USY 2 are more appropriate than NaY zeolite in FCC catalyst, and if density and acid strength of zeolites are improved and the surface acidity is reduced, the propagation reactions proceeding in the pores are enhanced, and the coke formation is greatly reduced. Furthermore, since coke precursor formed on the strong acid sites, FCC catalyst containing zeolite Y modified with rare earth and boron may contain less coke.
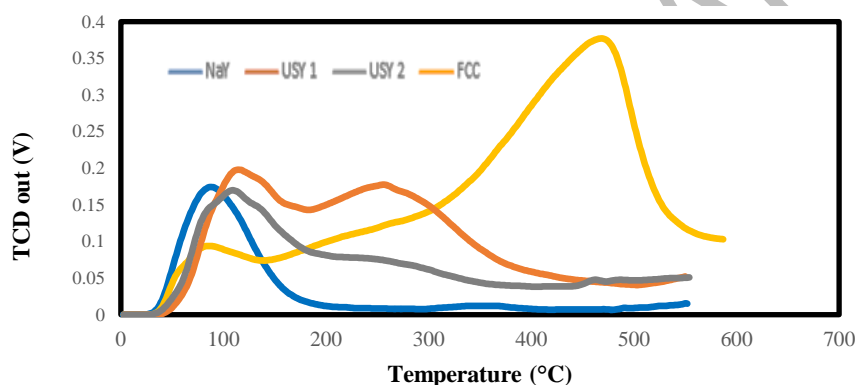

Fig 3. The TPD peaks of NaY, USY 1, USY 2, and FCC catalyst.

Scanning Electron Microscopy (SEM):

It is very important understand the changes in the morphology and chemical composition of the zeolite and catalyst surface. Definitively these structural and chemical changes affect the catalyst performance. The morphology of the samples has been widely studied by using microscopic and elemental imaging techniques such as scanning electron microscopy (SEM). Micrographs were produced at specific magnifications of 500x, 250x, 5kx, and 2kx to show the surface morphology of the FCC catalyst sample. Fig. 4 a and b show the morphology (mag. 500x and 250x) of spherical shape of the catalysts, with considerable variation in particle size. Fig. 4c and d (mag. 5kx and 2kx) revealed granular crystalline microstructure surface and fine granular crystalline micrographs which are in good agreement with BET results to indicate the distribution of contaminant metals on the FCC catalyst surfaces. Particles of FCC measure on average 80 µm in diameter. With progressing deactivation, the initially smooth-surfaced and surface-porous particles undergo a gradual textural transformation and develop a surface comprised of nodules and valleys [27].
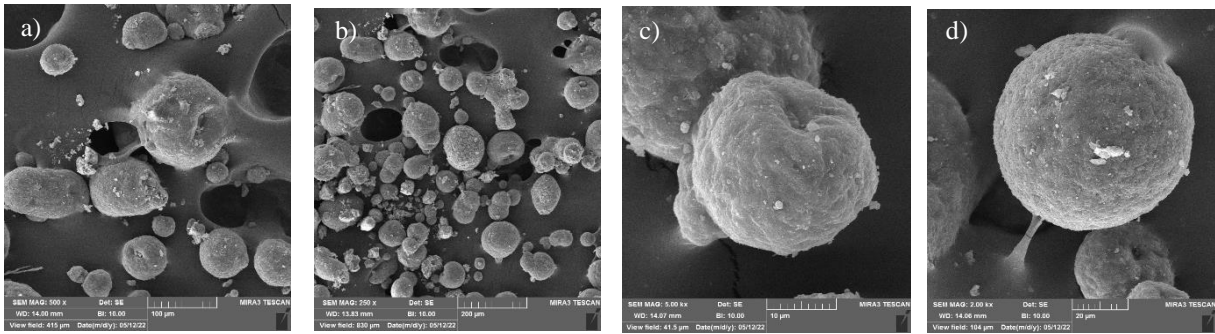
Fig 4. The SEM images of FCC catalyst sample at a) 500x, b) 250x, c) 5kx, and d) 2kx magnifications.

Fig. 5 a, b, and c show the FESEM images of NaY, USY 1, and USY 2, respectively. Micrographs were produced at specific magnification of 100 x. As can be seen, in Fig. 5 a, the powdered micro NaY zeolite crystals have a regular cubic shape and the average size of 5.22 mm. The most striking feature observed in USY 1 and USY 2 is their morphological similarity of them to the NaY sample. These micro-meso crystals have cubic shaped particles with an average size of 5.16 and 4.79 mm, respectively [28].
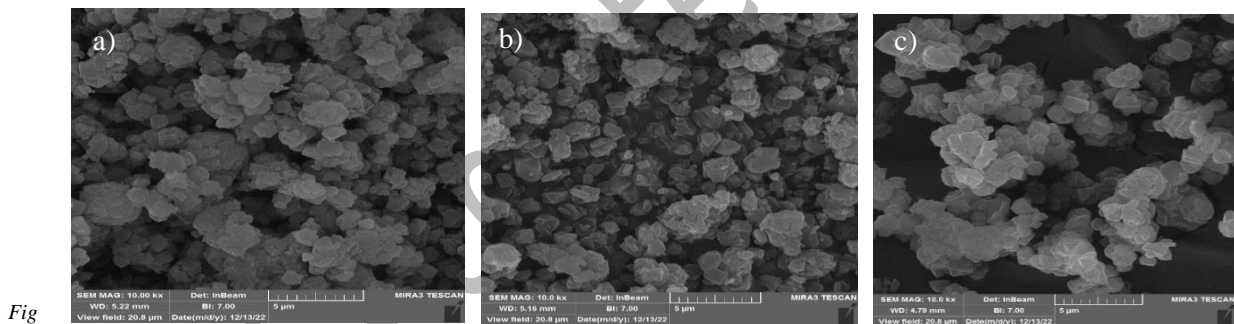
Fig

5. The SEM images of a) NaY, b) USY 1 ,and c) USY 2 at specific magnifications of 100x.

Micro Activity Test (MAT):

To evaluate the FCC catalysts a micro activity test (MAT) has been typically performed. The test consists of passing a given volume of feed over a heated catalyst and collecting both the gas and liquid products. Based on the product analysis, the conversion and selectivity are calculated. Table 3 revealed the conversion, and gasoline yield of the FCC catalyst produced by USY zeolites which indicates all results complied with the demand for the high micro-activity index of the FCC with the features of high strength, large specific surface area, large pore volume, and high catalytic activity. On the other hand, to further investigate and confirm the modifications techniques, the MAT test was also performed on the FCC catalyst with zeolite NaY zeolite modified with NH_4Cl, H_2SiF_6, and steam. For conversion and gasoline yield, 68.5 and 45.1 were obtained, respectively. As inferred from the results, a high conversion and gasoline yield were observed due to the characteristic catalytic property which was caused by USY zeolites. This leads to increasing the efficiency of the final product and its wide application.

Table 3. The conversion, gasoline yield, and coke selectivity of the FCC catalyst

FCC Catalyst		Unit	*Industrial index*
Conversion	76.53	*wt%*	≥74
Gasoline yield	52.03		-

Thermogravametric & CHN Analysis:

Analysis of the TGA and CHN results allowed us to measure the coke content of spent FCC which is deposited on the catalytic sites as a side-product of catalytic cracking due to hydrogen transfer reactions. Coke has unfavorable effects on the catalyst activity and selectivity via covering the acid sites and blocking the pores, which limit the accessibility of the reactant molecules to the active sites of the catalyst. The activity of FCC catalysts was found to fall exponentially with coke content, and it could recover most of its initial value. The TGA curve for the spent FCC catalyst containing the USY zeolites is shown in Fig. 6 which reveals compounds physicochemical and thermal properties. As shown in Fig. 6, three different degradations were observed over the range of 80-1000 °C. The first and second weight loss (3.5%) which belongs to delocalized waters and also dehydration of OH functional group continues up to the temperature of 250 °C in the FCC cavities continues up to the temperature of 150 °C. The third weight loss with a percentage of about 0.66% in the region of 250-400 °C displays the content of coke. And finally, the last degradation results from the decomposition of FCC catalyst with the sharp decrease between the ranges of 420-800 °C. It reveals a weight loss of approximately 3% which shows the percentage of localized waters. These results indicate FCC catalyst is successfully modified by rare earth, boron, acid, and steam and also with the outcome of their high thermal stability. Additionally, a low amount of coke in the spent FCC catalyst enables it to produce the large quantities of a light distillate (cracked) in the process without the addition of hydrogen. This amount of coke is less than the FCC samples that do not contain USY [12], and as a result, it has increased its capability and efficiency. On the other hand, since FCC coke is very complex, CHN analysis was used for the determination of coke composition and structure. This technique like TGA can be used for the characterization of coke on the solid catalysts. Results showed that the coke amount in FCC catalyst was about 0.62 by CHN analysis which is in accordance with the result of TGA result. This amount of coke is less than the FCC samples that do not contain USY zeolites, and as a result, it has increased its capability and efficiency.
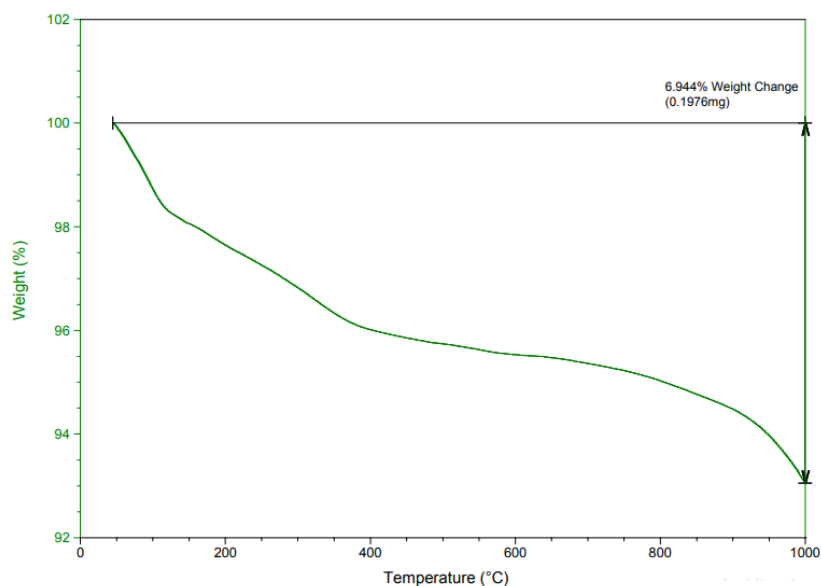
Fig 6. TGA curves of the spent FCC containing the USY zeolites.

CONCLUSIONS:

The key objective of this study was optimizing and modifying the NaY zeolite samples through different methods. Chemical modification was performed by adding rare earth and boron to the NaY zeolites as an extra-framework element and then placing them in the FCC structure simultaneously by increasing the Si/Al ratio with a large steamed unit cell parameter. Hydrothermal and acidic treatments with steam and H_2SiF_6 were used to obtain hierarchical zeolites with good hydrothermal stability, high acidity, and high strength in the pores of Y zeolites. The micro-mesoporous (hierarchical) USY zeolite with the advantages of improved accessibility to acid sites is a highly desired catalytic material for oil refineries. Both the acid concentration and acid strength of USY zeolites are high, which could be used for catalytic cracking performance. Actually, this kind of modification can direct more hydrocarbons to enter the pores through surface cracking reactions, and can improve the gasoline yield effectively. According to the expected behavior of two types of USY zeolites, comprehension of specific surface area and total pore volume on the amount of silica (SiO_4) and alumina (AlO_4) by using combined XRF, XRD, and N_2-porosimetry analysis, revealed the formation of porous zeolite crystal in its sodalite cage and the appropriate Si/Al ratio value in the final micro-mesoporous FCC product. Some other techniques such as ICP-OES, SEM, TGA, CHN, MAT, and TPD strongly confirm that FCC catalyst containing this kind of USY zeolites has more ability for conversion technologies in the refinery with less coke production and improved yield effectively. In fact, the modification of USY zeolites with boron and REE through various hydrothermal techniques could increase the moderate acids and thereby cracking activity while decreasing the strong acids of the zeolite. Further, the assessment results indicated that the FCC catalyst obtained by these USY zeolites simultaneously has more acidity, selectivity, conversion, yield, and less coke compared with the other formulation of the FCC catalysts.

Future outlook

Based on the successful entry of the Y zeolites into the industrial scene, zeolites quickly found many applications in petroleum processing in subsequent years; however, catalytic cracking still by far is the largest volume of zeolite catalyst consumer worldwide. Today, fluid catalytic cracking (FCC) catalysts account for more

than 95 % of the global zeolite catalyst consumption (primarily USY zeolite). Fluid catalytic cracking units (FCCUs) around the world currently process around 15 million barrels per day and constitute the main conversion process in a typical fuels refinery. So, as a result, the modifications made in the samples of zeolite Y can be very effective in the FCC catalyst industry.

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