



DEVELOPING AN EFFICIENT CATALYST BASED ON THERMAL AND ACID-TREATED CLAY FOR THE REMOVAL OF TRACE OLEFINS FROM AROMATIC COMPOUNDS

NOOSHIN NOURI¹, MAHBOUBEH TASVIRI^{2*} , AND HOSSEIN GHASEMZADEH¹

¹Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran

²Department of Physical and Computational Chemistry, Faculty of Chemistry and Petroleum Sciences, Shahid Beheshti University, Tehran, Iran

Abstract—Bentonite is used as a catalyst in the removal of olefins from aromatic compounds and the present study was designed to investigate how its performance might be improved by various treatments. Bentonite from Semnan mine, Iran, was used in the study following initial characterization. In order to investigate the effect of acid and thermal treatments on the removal of olefins from aromatic compounds, bentonite samples were modified using HNO₃ at different concentrations (0.15, 0.3, 0.5, 0.7, 1, and 2 M) and were also at temperatures between 100 and 340°C for 3 h. To examine the catalytic activity of bentonite-based catalysts, the samples were evaluated after running batch and continuous experiments. The optimum catalyst was characterized using thermo-programmed desorption (TPD) of NH₃ to examine the acidic sites. Scanning Electron Microscopy (SEM) images, nitrogen adsorption-desorption isotherms (BET analysis), and X-ray diffraction (XRD) patterns were used to study the structural changes of the bentonite produced by the acid and thermal activation. The removal of olefins by the catalysts in batch and continuous systems revealed that the sample modified with 0.3 M Nitric acid at 150°C had superior catalytic activity, with olefin conversion remaining at >50% for up to 20 h. Nitrogen adsorption-desorption isotherms showed that acid treatment can produce a mesoporous structure. On the other hand, the TPD analysis indicated that during weak acid treatment, some cations, such as Al³⁺ and Fe³⁺, were leached from octahedral sheets and the interlayers of the clay mineral resulting in weak acid sites being generated. Finally, a novel method was proposed and tested for measuring the Bromine Index (BI) using potentiometric titration.

Keywords—Acid treatment · Aromatic compound · Bentonite · Bromine Index · Olefin removal

INTRODUCTION

Aromatic hydrocarbons, especially benzene, toluene, and xylene (BTX), play a significant role in the petrochemical industries. These compounds are primary feedstock in producing materials such as synthetic rubber, detergent, dyes, and intermediates (Franck and Stadelhofer 1988). The BTX compounds are produced using reformat, pyrolysis, or cracking (Genuino et al. 2019). These processes lead to the formation of trace amounts of undesired compounds in the form of olefins, which, even in concentrations as low as a few parts per million, can have an adverse effect on the quality and application of the aromatics (Tian et al. 2012). Removing these small amounts of olefins from aromatic compounds is essential. Modified clay can be used for this purpose because of its specific physical and chemical features, namely large specific surface area, thermal stability, and the existence of acid centers (Sulikowski 2006; Centi and Perathoner 2008; Roth et al. 2016).

Bentonite consists essentially of montmorillonite, which is generally classified into sodium (Na) or calcium (Ca) types depending on the dominant exchangeable ion (Eisenhour and Brown 2009). Bentonite is valued for its sorption properties, which originate from its large specific surface area, swelling capacity, and cation exchange capacity (CEC) (Sulikowski 2006; Centi and Perathoner 2008; Roth et al. 2016).

Currently, in order to prepare clays as efficient catalysts for catalytic reactions, they are modified by various methods, including thermal, acid, and pillaring processes (Kloprogge 1998; Lagaly 2006; Noyan et al. 2007). Acid treatment is one of the conventional approaches for modification of clay with the aid of some mineral acids, such as sulfuric acid, hydrochloric acid, and nitric acid (Madejová et al. 2009). The acid treatment produces some acidic sites, which make the clay suitable for particular catalytic reactions (Noyan et al. 2007; Salem and Karimi 2009). The effect of thermal and acid pretreatment on the surface acidity and catalytic activity of Jordanian bentonite in the tert-butylphenol in the tert-butylphenol was studied by Mahmoud et al. (2003). Acid-treated bentonite samples possess more acidic sites than untreated samples. The Hammett acidity function, H_0 , was used by Mahmoud et al. (2003) as a measure of the acid strength; the smaller the H_0 value, the stronger the acid. The maximum number of acid sites ($H_0 < 4.8$) was obtained when Jordanian bentonite was treated with 0.1 M H₂SO₄, H₃PO₄, or HCl. Treating the clay samples with 1.0 M H₂SO₄, 1.0 M H₃PO₄, or 0.1 M HCl generated a maximum concentration of strong acidic sites ($H_0 < 3.6$). Compared to weak acid sites, strong acid sites ($H_0 < 2.9$) produced appreciable enhancement of the debutylation rate. The catalytic performance of allophane, palygorskite, and sepiolite in the dehydration and conversion of alcohols to ethers was measured by Marosz et al. (2020). For this purpose, clay mineral samples were acid-treated (0.8 M HNO₃; 95°C; 2, 8, or 24 h) and, after calcination (500°C; 6 h), tested as catalysts for the conversion of methanol

* E-mail address of corresponding author: m_tasviri@sbu.ac.ir

DOI: 10.1007/s42860-020-00108-3

© The Clay Minerals Society 2020

to dimethyl ether and for the conversion of ethanol to diethyl ether and ethane. During acid treatment, the BET surface area, pore-volume, and surface acidity for the sepiolite and palygorskite series of samples increased significantly. In contrast, the BET surface area, pore-volume, and surface acidity for the allophane series showed a decrease in the process of acid treatment. In a typical experiment of acid treatment for 24 h, the surface area (S_{BET}), pore volume (V_{total}), and surface acidity (SA) of raw allophane vary from $183 \text{ m}^2 \text{ g}^{-1}$, $0.150 \text{ cm}^3 \text{ g}^{-1}$, and $267 \mu\text{mol g}^{-1}$ to $171 \text{ m}^2 \text{ g}^{-1}$, $0.144 \text{ cm}^3 \text{ g}^{-1}$ and $143 \mu\text{mol g}^{-1}$, respectively. Among the samples studied, allophane was the most catalytically active in the dehydration of methanol to dimethyl ether (at a temperature of 350°C , methanol conversion was $>80\%$). Unlike other samples, acid treatment increased the catalytic activity of allophane.

An attempt was made by Pu et al. (2012) to improve the catalytic activity of a commercial clay by adding zeolite (MCM 22) and lanthanum. This modified catalyst showed a significant superiority over the commercial clay, and the laboratory and industrial tests revealed that the modified catalyst demonstrated noticeably better durability than the commercial clay. Based on the TPD profile results, the modified commercial clay had many weak Lewis acid centers compared to the commercial clay due to the presence of zeolite. The weak Lewis acid centers are thought to play a significant role in the alkylation of olefins and purification of aromatics. Also, the synthesized catalyst did not change the quantity or distribution of the aromatic hydrocarbons.

In another investigation, palygorskite (Plg), a naturally fibrous hydrated aluminum-magnesium silicate mineral, was used as an efficient catalyst in the olefin-removal reaction. The Plg-supported catalyst surface area and pore structures were improved by acid activation. In addition, various metal halides were applied to improve further the surface acidity of the catalyst obtained. The experimental results in a batch autoclave indicated the sample modified by 21 wt.% of sulfuric acid and CoCl_2 with a loading content of 7 wt.% showed the greatest olefin conversion of 92.1% (Guo et al. 2020).

The present study aimed to modify the bentonite surface by optimizing the acid concentrations and calcination temperatures to prepare an enhanced catalyst for alkylation reactions, to determine the optimum parameters for removing olefins from aromatic compounds efficiently, and to develop a suitable method for measuring the Bromine Index (BI) by potentiometric analysis.

EXPERIMENTAL

Materials and Methods

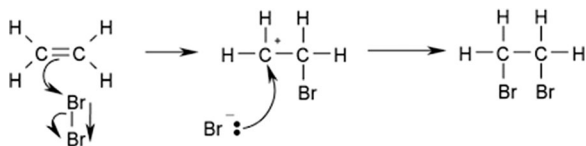
Raw bentonite as the primary material, with a CEC of 0.9 meq g^{-1} and a specific surface area of $33.28 \text{ m}^2 \text{ g}^{-1}$, was purchased from Abtin Shimi Co. (Semnan, Iran). It had the following major-element chemistry: 66% SiO_2 , 0.24% Na_2O , 2% MgO , 9.5% Al_2O_3 , 1.8% K_2O , 1.1% Fe_2O_3 , 3% CaO , 0.36% other, and 16% LOI. In order to study the catalytic activity, bentonite was powdered by laboratory dry milling equipment to middle-size (-100 to $+200$ mesh). The powders obtained were dried in a laboratory oven at 105°C .

Other chemicals were purchased from Merck Chemical Co. (Darmstadt, Germany). All the reagents were of analytical grade. The aromatic compounds (Table 1) and details of their characteristics were obtained from Nouri Petrochemical Co. (Bushehr, Iran). The Bromine Index (BI) of the aromatic hydrocarbons was $\sim 140 \text{ mg of Br}_2/100 \text{ g}$, a level which poses significant difficulty to industry.

BI Measurement of Feedstock and Products by a Potentiometric Method

Bromine Index (BI) is considered to be an indicator of olefin content in aromatic compounds, and is defined as milligrams of bromine consumed by 100 g of a hydrocarbon sample. A small BI indicates the presence of a small amount of olefins in aromatic compounds. In contrast, a large value for BI demonstrates that the aromatic compounds contain a significant amount of olefins (Chen et al. 2009).

The BI of the samples was determined by potentiometric titration, which is based on reaction 1:



Reaction 1 was carried out by adding $\text{Br}_{2(\text{sol})}$ as a titrant (Table 2) to the mixture of composition A (Table 2) and 4 g of autoclave outlet (with the components mentioned in Table 1) with constant stirring of the solution at room temperature. The olefin double bonds were detected and broken by Br_2 molecules (Reaction 1) to consume all the double bonds. The bromine concentration increased gradually in the solution while the olefins decreased, leading to a gradual increase in the potential. Note that the Br_2 required for the titration mentioned above is produced according to reaction 2:

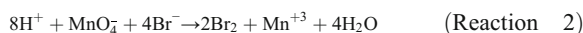


Table 1. Components of the aromatic hydrocarbon

Component	Amount (wt.%)
Non-aromatic	6.38
Benzene	7.85
Toluene	21.37
Ethylbenzene	12.8
<i>p</i> -Xylene	7
<i>m</i> -Xylene	24.54
<i>o</i> -Xylene	8
C9 and C9+ aromatics	12.08

Table 2. Components in the titrant and Composition A

Components in the titrant (1 g of titrant solution with ~0.4 mg of Br ₂ (sol))	wt. %
Acetic acid	82%
1 M KBr-solution	16%
KMnO ₄ (sol) 1%	2%
Composition A	wt. %
Acetic acid	63%
Methanol	21%
1 M KBr-solution	16%

The BI was calculated according to Eqn. 1, using the curve of potential vs. titrant mass, and the endpoint of this curve was obtained.

$$BI = \frac{0.4 \times m_{EP} \times 100}{xg \text{ sample}} \quad (1)$$

where m_{EP} is the mass of titrant in the endpoint of the titration curve, and x is the mass of autoclave outlet or continuous system (Fig 3).

The efficiency and accuracy of the method were appraised by a standard solution with a BI of ~100 mg Br₂/100 g (0.088 g of 1-decene was weighed and poured into a sample container; then the total mass was increased to 100 g by addition of pure toluene). The final solution was titrated through the potentiometric method. The measured BI was ~100 mg Br₂/100 g which proved the accuracy of the method.

Preparing Titrant and Analyte for Potentiometric Analysis

Titrant and analyte solutions were prepared for BI measurement of the feedstock and products via potentiometric analysis. For this purpose, 50 g of titrant was prepared by adding 1.064 g of 1 wt.% potassium permanganate solution to the mixture of acetic acid and potassium bromide solution (Table 2).

Acid Activation of Clay

Raw bentonite was treated with nitric acid solutions at various concentrations, namely 0.15, 0.3, 0.5, 0.7, 1, and 2 M. The suspensions were stirred for 2 h at 70°C (which are the optimum contact time and temperature, respectively (Fig. 1)), and then washed several times with distilled water. The mixture was filtered and dried at 100°C overnight. Then, to investigate the thermal treatment, the mixture was heated at 100, 150, 200, 270, and 340°C for 3 h to obtain the final solid acid-treated catalysts.

Optimization of Treatment Conditions for a Sample Modified with 0.3 M HNO₃

The effects of the activation temperature and the activation time in the acid treatment step on the olefin conversion were investigated by the single-factor experiment method (Fig. 1). The process was performed in a batch system with reaction conditions as listed in Table 3 and in the presence of the sample modified with 0.3 M HNO₃. In the acid treatment of clay, by increasing the activation temperature and time, the BI decreased, reaching a minimum for temperature = 70°C and time = 120 min, and then rose slightly to a constant value (Fig. 1a,b). The specific surface area was increased with an increase in activation temperature and activation time in the acid treatment.

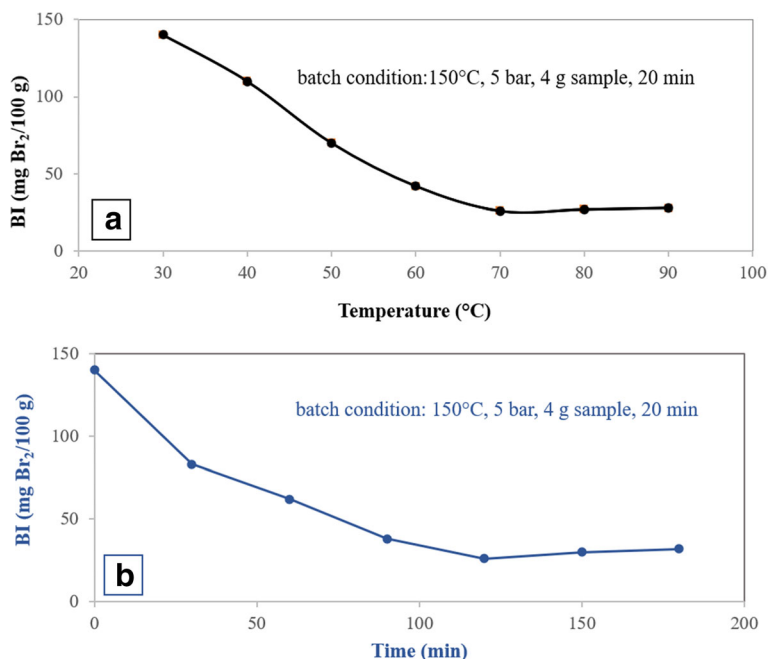


Fig. 1 Optimization conditions for acid treatment of bentonite for olefin removal from aromatic hydrocarbons using the sample treated with 0.3 M acid in the batch system. **a** Reaction temperature. **b** Reaction time

Table 3. Parameters for the batch system. (t_{RT} is the time period during which the catalyst was in contact with the feedstock.)

Temperature (°C)	t_{RT} (min)	Pressure (bar)	Clay (mL)
150	20	5	6

The specific surface area reached a maximum value at 70°C and 120 min (Fig. 2a,b).

Catalytic Tests in the Batch System

The catalytic activity tests in the batch system (Fig. 3a) were carried out in an autoclave, equipped with a stirrer, nitrogen cylinder, and a controlled heating system to maintain the required temperature. The parameters are the same as the parameters of the continuous systems (Table 3). 4 g of activated clay sample along with 100 g of feedstock was poured into the autoclave. The autoclave was connected to the N₂ cylinder to keep the pressure of the system at 5 bar and to reduce the boiling point of aromatic compounds. The temperature of the autoclave was fixed at 150°C for 20 min under stirring conditions. Afterward, the N₂ (gas) was purged. The outlet fluid was filtered to separate the acid-activated sample from the feedstock, and then it was titrated to find the BI.

Catalytic Tests in the Continuous System

A continuous system was employed to evaluate the efficiency and lifetime of the activated clay. To this end, 4 g of activated clay was packed between two alumina grains of sand (40–60 mesh), and then placed in the reactor. The reaction temperature was ~150°C, the reaction pressure was 5 bar, and the liquid hourly space velocity (LHSV) was 20 h⁻¹. Accurate temperature uniformity was achieved through three zones of

the thermal furnace, which controlled the temperature inside the reactor. Three sets of thermocouples recorded the temperature of the middle zone. The temperature of the reaction zone was kept at 150°C by a temperature-control system connected to computer *JUMO* software. An Eldex Laboratories Inc (Napa, California, USA) pump (Optos Model 1SMP) was used to pump inlet feedstock into the reactor.

The schematic representation of the reactor is divided into three thermal regions (Fig. 3b). The catalyst was loaded in the middle part of the reactor. In order to determine the BI content, 4 g of the sample was withdrawn from the reactor output at 1 h time intervals. The olefin conversion was calculated according to Eqn. 2:

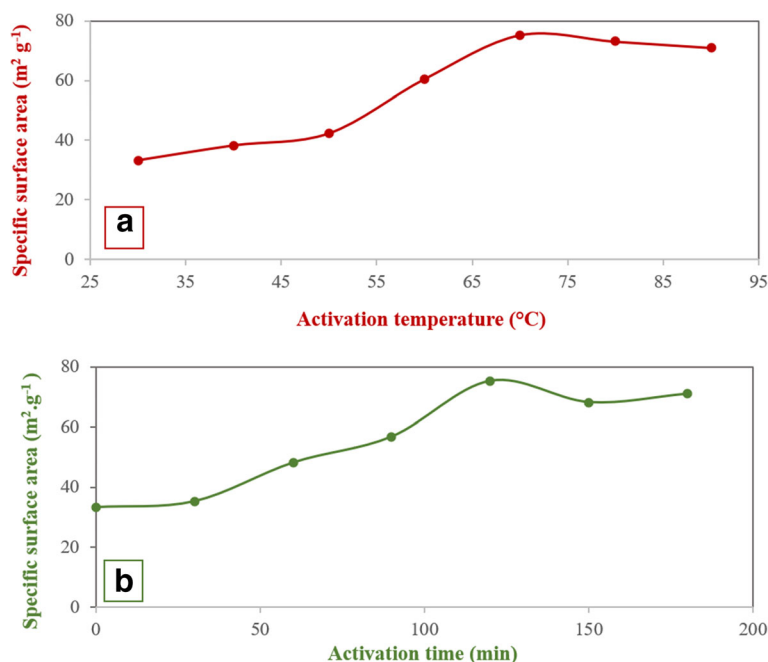
$$\%Y = \frac{BI_0 - BI}{BI_0} \times 100 \quad (2)$$

where BI₀ and BI correspond to the Bromine Index of raw materials and effluent liquids of the reactor, respectively.

Characterization

The XRD patterns of the samples were recorded using a Philips-PW-1800 diffractometer (Watertown, Connecticut, USA). The measurements were performed at 40 kV and 40 mA over the range 10–80°2θ with a step size of 0.02°2θ, using CuKα radiation ($\lambda = 1.54056 \text{ \AA}$). The elemental composition of the samples (dried at 100°C for 6 h before testing) was measured by X-ray fluorescence (XRF) (SPECTRO XEPOS, Kleve, Germany) using an excitation current of 50 mA, an excitation voltage of 50 kV, and with a sensitivity of 0.001%.

The surface acidity of the catalyst was determined by temperature-programmed desorption (NH₃-TPD) using a CHEMBET-3000 apparatus (Quantachrome Company,

**Fig. 2.** The effect of **a** activation temperature and **b** activation time on the specific surface area of bentonite in the presence of 0.3 M HNO₃

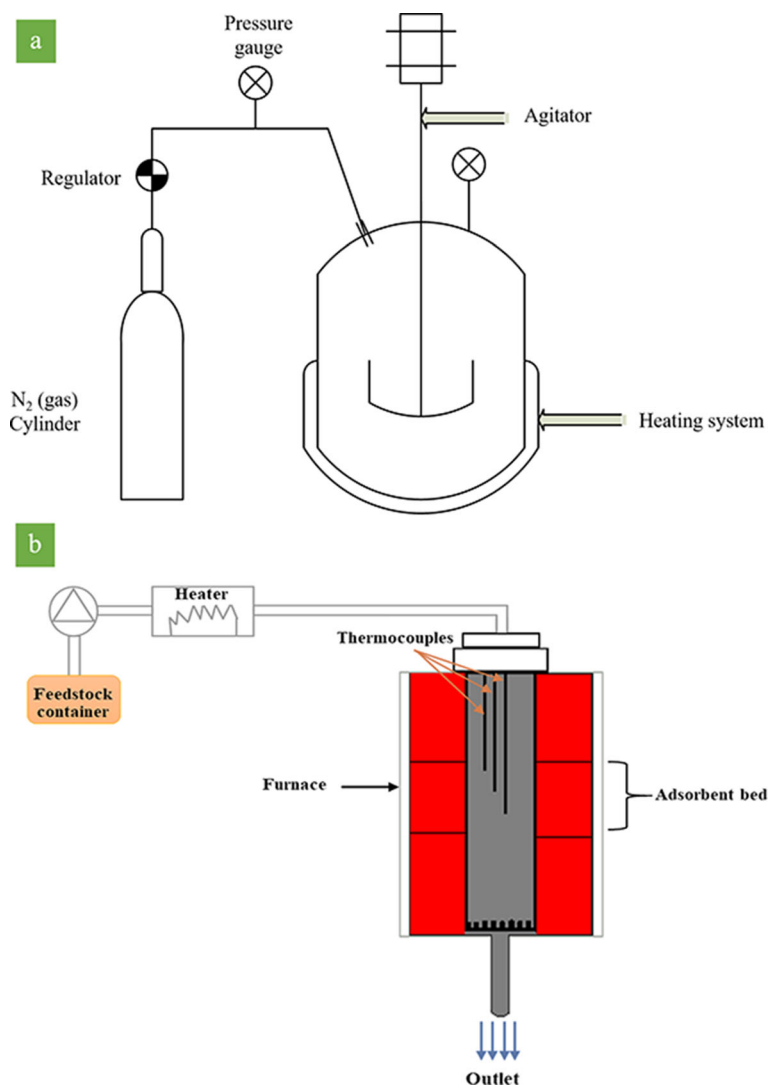


Fig. 3. Schematic representation of the reactor in **a** batch and **b** continuous systems

Graz, Austria). In this method, 0.1 g of the sample was placed in a tubular reactor. The sample was cleaned by He flow (30 mL min^{-1}) from room temperature to 800°C for 10 min. Then, it was cooled to 100°C and saturated with NH_3 gas for 30 min. The physisorbed ammonia was removed by passing He over it at 100°C . Finally, the samples were heated from 100 to 800°C , and the ammonia evolved was analyzed using an online TCD (Trombetta et al. 2000; Chen et al. 2009; Alsawalha et al. 2011).

The textural parameters of the samples were determined by N_2 adsorption-desorption measurements at 77 K using an ASAP 2010 instrument (Micromeritics, Norcross, Georgia, USA). Prior to the analysis, the samples were outgassed under vacuum at 200°C for 6 h. The specific surface area of the sample was measured using N_2 adsorption-desorption isotherms. BET analysis provides precise specific surface area evaluation of materials by nitrogen adsorption measured as a function of relative pressure. The surface area is determined by

calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface of the material. The technique encompasses external area and pore area evaluations to determine the total specific surface area. BET is used to determine a range of disperse, solid microporous to mesoporous materials. Barrett-Joyner-Halenda (BJH) analysis can also be utilized to define pore area and specific pore volumes through adsorption and desorption techniques (Barrett et al. 1951).

RESULTS AND DISCUSSION

Effect of Acid Concentration

The activities of clays which were acid-activated in various ways were investigated in both batch and continuous systems. Experimental measurement of the batch system (Fig. 4a) revealed that the sample treated with 0.3 M HNO_3 demonstrated better activity than other samples because the output fluid of the autoclave consumed a small amount of

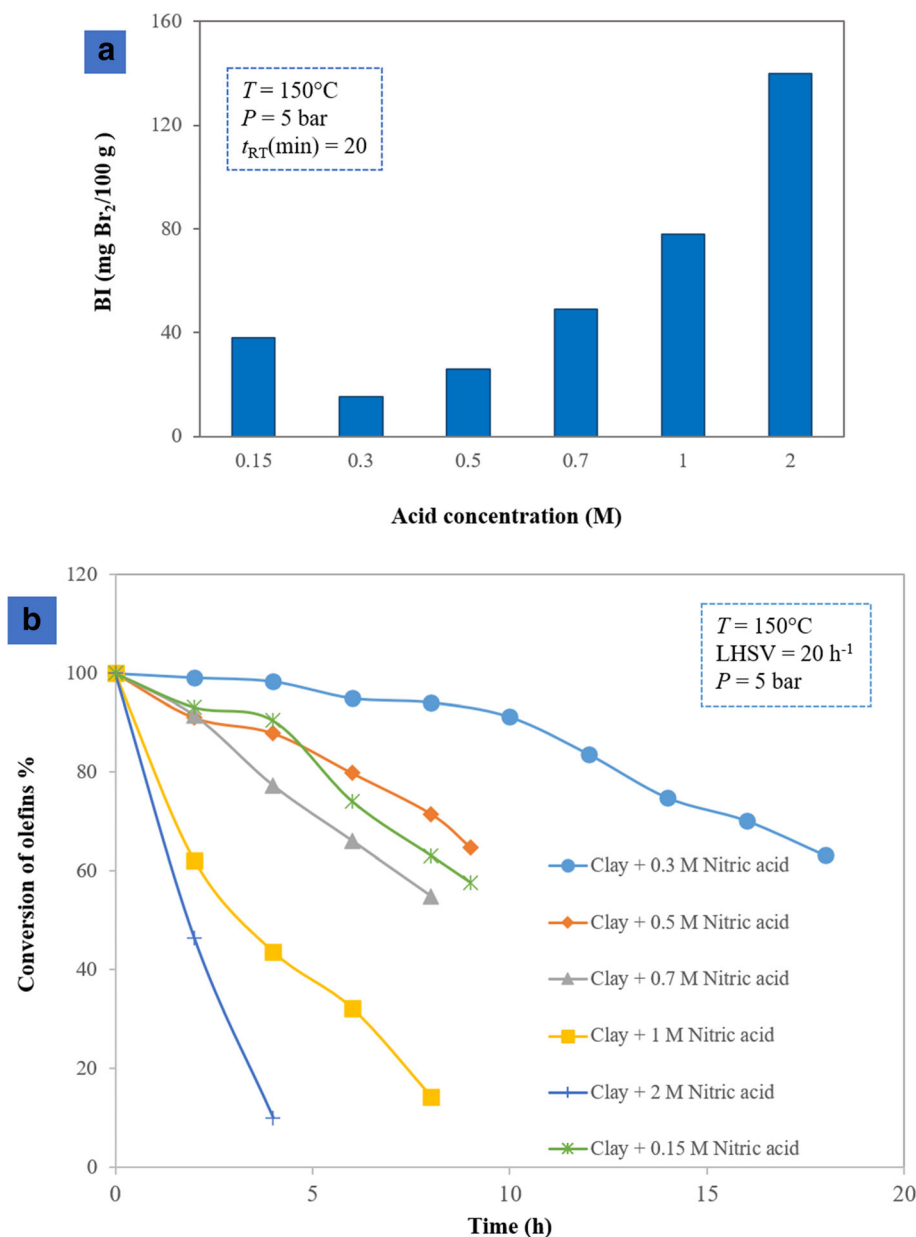


Fig. 4. Olefin conversion over the acid-treated catalysts with various concentrations in **a** batch and **b** continuous systems

Br₂ in the potentiometric analysis. It contained a small amount of the olefins as a result. Next, the activity of the acid-activated samples was evaluated in the continuous system (Fig. 4b). At the initial time, before the addition of any catalyst (BI = 0), the conversion percentage was maximum, according to Eqn. 2. During the reaction, various acid-activated samples showed different activities at removing olefins and consequently had different BI values. According to Eqn. 2, various conversion percentages were achieved, among which the sample modified with 0.3 M HNO₃ had >50% catalytic activity for 20 h, whereas other samples showed less activity in olefin conversion. During

acid treatment, some exchangeable cations (K⁺, Na⁺, and Ca²⁺) were replaced by hydrogen ions, and some cations such as Al³⁺ and Fe³⁺ were leached from the octahedral and tetrahedral sheets, with some located in the interlayer of the clay mineral and producing acid sites. At high concentrations of nitric acid (2 M and 1 M), cations such as Al³⁺ and Fe³⁺ were leached dramatically from the octahedral sheets. These cations, therefore, could not provide the clay with acid sites. In a low acid concentration (0.15 M), cations could not be extracted effectively from the octahedral sheets and, as a result, the sample demonstrated low activity in terms of olefin removal (Pu et al. 2012).

Effect of Temperature on Reducing the BI

In the next step and to enhance the clays further, the optimum acid-activated clay, modified with 0.3 M HNO_3 , was treated at various temperatures. The results of batch (Fig. 5a) and continuous (Fig. 5b) tests demonstrated that the optimum acid-activated clay at a temperature of 150°C was best at reducing the amount of olefins in aromatic compounds. Acid-activated clay had both Lewis and Brønsted sites, where the Brønsted acidity derived from the dissociation of water molecules in the hydration sphere of the interlayer exchangeable

cations (Eqn. 3), and Lewis acidity was usually associated with exposed Al^{3+} and Fe^{3+} at the broken crystallite edges of clay minerals, and such acidities can be increased by heating the clay. The hydrogen state of the clay mineral determines the total acidity and ratio of Brønsted to Lewis sites. In the activated clay, Si-OH-Al groups as Brønsted sites were stronger than Al-OH-Al and Si-OH-Si. The acidity of Si-OH-Al groups was influenced enormously by drying (Lagaly 2006; Chen et al. 2009). Heating the clay led to the elimination of the interlayer water and exposed more acidic sites to the reactant. Based on

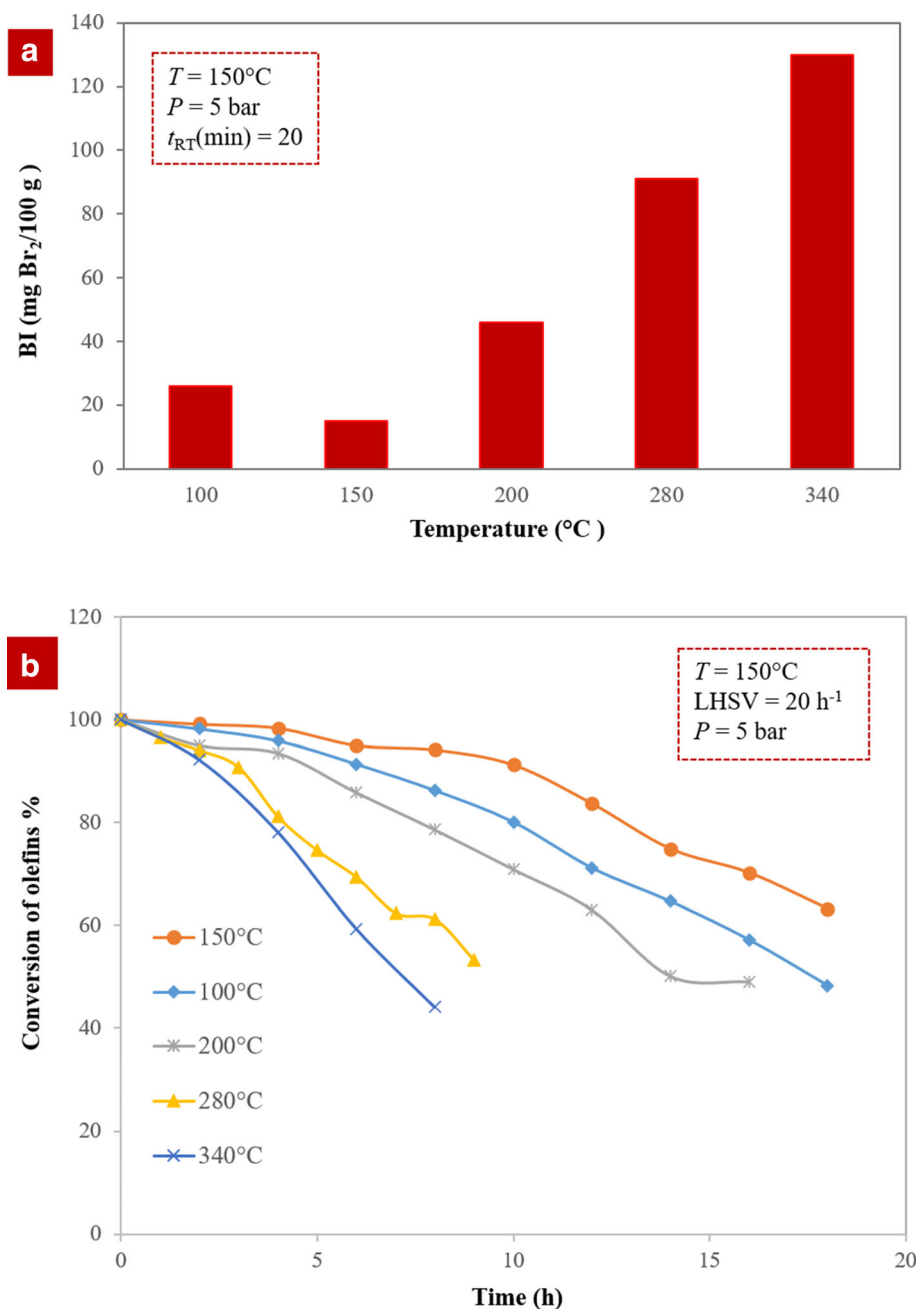


Fig. 5. Olefin conversion over the thermally treated catalysts with various temperatures in **a** batch and **b** continuous systems

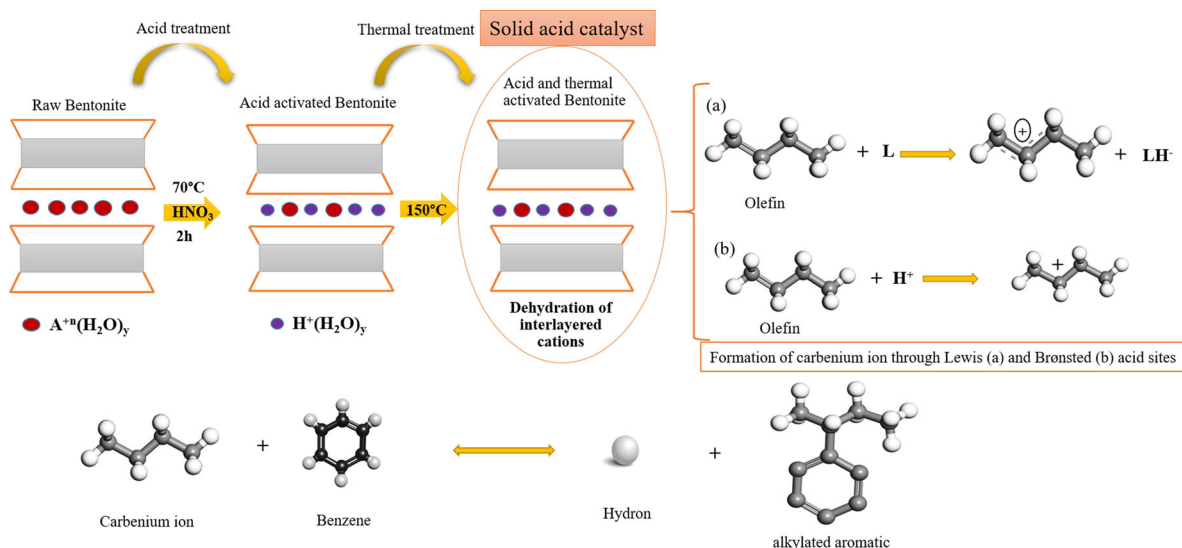
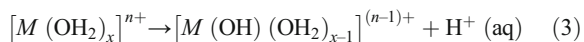


Fig. 6. The reaction between olefins and aromatics

the results of the batch and continuous systems, most of the interlayer water evidently was driven out at 150°C. Consequently, the modified sample provided more accessible acid sites for olefin reactions. Although higher temperatures (>300°C) removed the interlayer water and dehydrated the metal cations in the interlayer, it led to the irreversible collapse of the clay layers (Bradley and Grim 1951). Because catalyst activity depends significantly on the amount of water available between the layers, thermal treatment was considered to be a crucial factor

The Friedel-Crafts alkylation of benzene with olefins over solid acid catalysts is widely known to occur through the generally accepted carbenium-ion mechanism (Fig. 6). The olefin molecules are converted into a carbenium ion intermediate through the action of a Lewis (L) acid site and a Brønsted (B) acid site. Lewis acid sites accept hydride ions (H⁻) from an alkane, and Brønsted (B) acid sites attack π electrons of the olefin molecule. The unstable carbenium ion reacts with aromatics by an alkylation reaction. The desorption process and the loss of the hydron provide the alkylated aromatic and restores the acid sites (Guo et al. 2020) (Fig. 6).



XRD Analysis of the Samples

The mineralogical changes in bentonite before and after olefin removal reactions were determined by XRD of raw

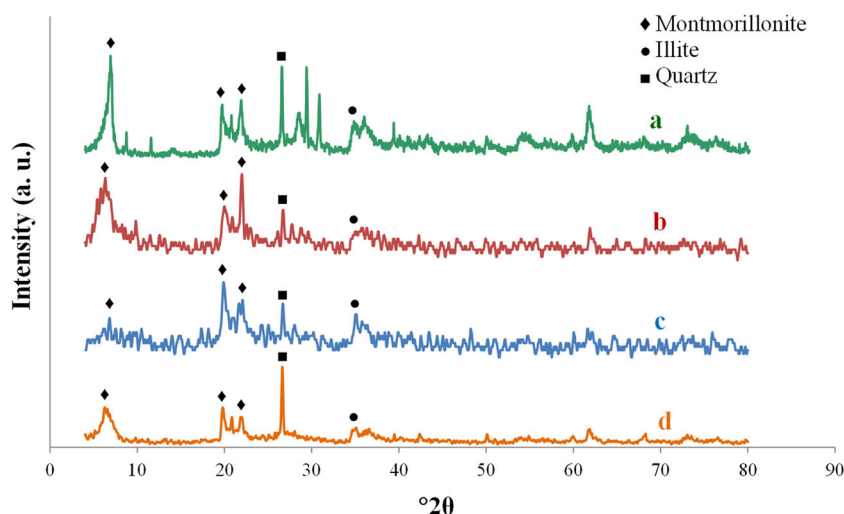


Fig. 7. XRD patterns of a raw bentonite, b optimum acid-activated sample before olefin removal reaction, c clay activated by 1 M HNO₃, and d optimum acid-activated sample after the olefin-removal reaction

bentonite and the optimum acid-activated sample. The XRD patterns demonstrated that bentonite has Ca-rich montmorillonite (d_{001} at $\sim 6^\circ 2\theta$) as the main clay mineral. The peaks that appeared at ~ 20 and $36^\circ 2\theta$ belonged to montmorillonite and illite. The XRD patterns revealed that the intensity of the peaks belonging to the main montmorillonite was decreased by HNO_3 activation, which indicated that the crystallinity of Ca-montmorillonite is affected considerably by acid activation (Fig. 7). More changes were observed by increasing the acid concentration due to the decomposition of the structure. X-ray diffraction patterns of the optimum sample after olefin removal (Fig. 7d) showed structural changes mainly in the quartz intensity at $27^\circ 2\theta$. The intensity of the peaks belonging to the montmorillonite at ~ 6 and $23^\circ 2\theta$ were also noted to decrease. The results indicate that the olefin-removal reaction did not have a severe effect on the catalyst structure, however.

TPD Analyses

The surface acidity of the catalyst plays an essential role in regulating the activity of the alkylation reaction. The total acidity of the raw bentonite as well as that of the acid-activated clay were measured before and after olefin removal by ammonia temperature-programmed desorption (NH_3 -TPD) (Trombetta et al. 2000). Weak and strong acid sites existed in the raw and optimum acid-activated clay at desorption temperatures of $<300^\circ\text{C}$ and $>450^\circ\text{C}$, respectively (Fig. 8). The raw bentonite showed a sharp peak at $\sim 670^\circ\text{C}$. In comparison, the optimum acid-activated clay exhibited two peaks at desorption temperatures of 230°C and 750°C , which can be related to two different types of active sites. Below 300°C , the weak coordination bands of ammonia with Lewis acid sites were broken, which led to the desorption of ammonia and the appearance of the first peak. Compared to the optimal sample, this peak was smaller for the raw bentonite, implying a very small number of weak Lewis acid centers. The peaks at $>450^\circ\text{C}$ were due to the strong Brønsted acid sites (Table 4). Acid activation causes a decrease in the intensity of the peak at $>450^\circ\text{C}$ for the optimal sample, whereas peaks at $<300^\circ\text{C}$ became stronger (Fig. 8). Weak Lewis acid sites were suggested by Pu et al. (2012) to play a crucial role in removing olefin. Acid treatment of clay at

Table 4. Acid-content distribution for the raw bentonite and for the optimal catalyst before and after reaction

Bentonite	Weak acid ($<300^\circ\text{C}$) (mmol/g)	Strong acid ($>450^\circ\text{C}$) (mmol/g)
Raw	None detected	4.1792
Before reaction	0.6953	3.2783
After reaction	0.6831	3.2581

a controlled value can, however, increase enormously the number of weak Lewis acid centers available for olefin alkylation. The surface acid sites of the sample showed no obvious differences after the reaction (Table 4). These observations lead to the conclusion that surface acid sites of the catalyst are secure during the process of olefin removal.

Surface Texture Analysis

The N_2 adsorption-desorption isotherms of the raw bentonite and the optimum acid-activated clay were measured using the ASAP 2010 instrument (Fig. 9). The isotherm for these samples was characterized as type IV based on the IUPAC classification, corresponding to mesoporous adsorbents, which have suitable porosity for the accommodation of aromatic molecules (Kooli et al. 2006). The hysteresis loops of the samples resemble the H_3 type, which indicated the existence of uniform aggregates of plate-like particles consisting of slit-shaped pores in the samples (Kumar et al. 1995; Kooli et al. 2006).

The results of TPD and N_2 adsorption-desorption analysis revealed that the surface acidity and textural properties of the clay were altered greatly by acid treatment (Murilo et al. 2018; Hao et al. 2019). A net negative electric charge on the surface of the clay formed by the substitution of trivalent and divalent ions of the octahedral and tetrahedral sheets is balanced either by Ca^{2+} or Na^+ . During acid treatment, a considerable amount of these ions can be removed and replaced by hydrogen ions. Bentonite also contains Fe^{2+} , Mg^{2+} , and Al^{3+} as the second group of cations that belong to the octahedral sheets (Güven 2009; Ross and Shannon 1926). Some of these ions in the

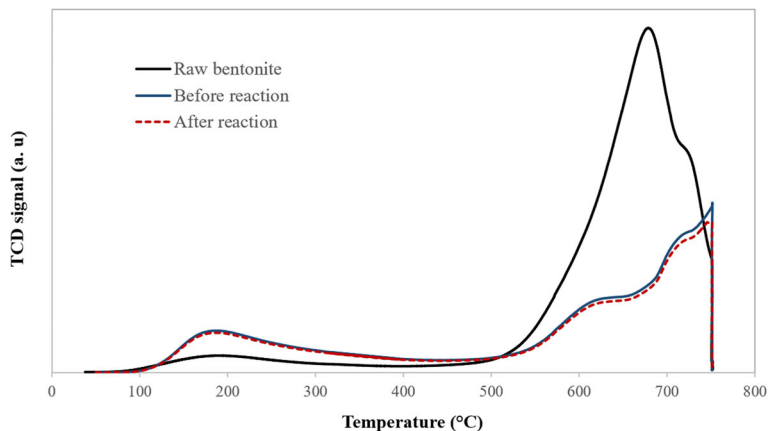


Fig. 8. Profiles of temperature-programmed desorption of ammonia for raw and optimum acid-activated bentonite before and after the olefin-removal reaction

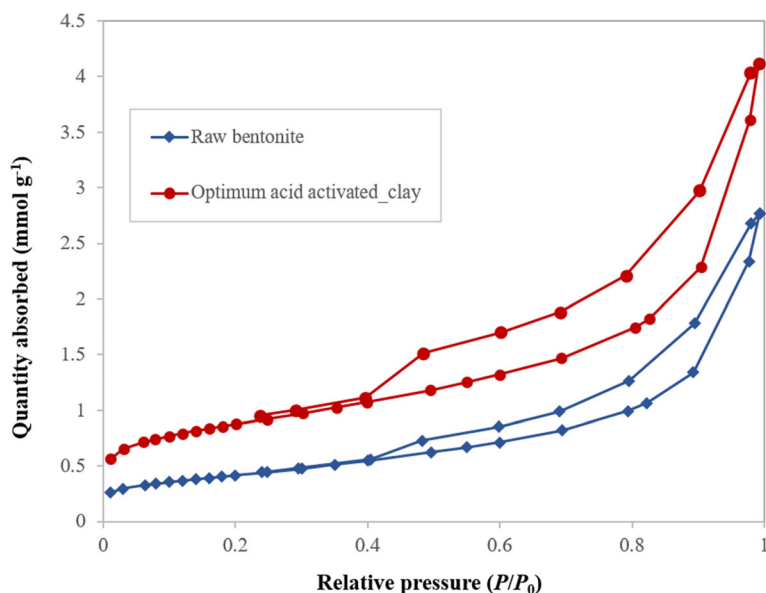


Fig. 9. N_2 adsorption/desorption isotherm for raw and acid-activated bentonite

octahedral sheets are dissolved out, leaving floppy silica sheets on acid modification. Folding of the sheet can make a mesopore, which has the ability to accommodate larger molecules for sorption and catalysis (Table 5) (Emam et al. 2008; Alothman, 2012). The results of N_2 adsorption-desorption analysis (Table 5) indicated that the acid treatment improved the textural properties of raw bentonite and provided suitable sites to accommodate aromatic molecules. Moreover, during the reactions and formation of reaction mixture-components the total pore volume and specific surface area of the catalyst decreased (Table 5).

Surface Morphology of Samples

The surface morphology of the modified bentonite was analyzed by scanning electron microscopy (SEM) to evaluate

the effects of acid and thermal treatment on the raw bentonite (Fig. 10). The results showed that the surface morphology of raw bentonite changed significantly during acid and thermal activation. The physicochemical reactions altered the morphology of the clay as the pores opened, and the clay surface appeared to be more porous and homogeneous. Acid activation followed by thermal activation provided more porous clay due to the removal of any water that was already present in the clay or which was adsorbed during the washing of acid-activated clay. From Fig. 10, it was observed that the bentonite particles were sub-angular, and that acid activation enhanced the specific surface area of the clay and led to significant mesoporosity (Amari et al. 2018). The irregular shape of the particles of the optimum sample before and after olefin removal showed no significant differences (Fig. 10b,c).

Table 5. Structural and textural parameters for the raw bentonite and for the optimum modified bentonite before and after the olefin-removal reaction

Bentonite composition and properties	Raw	Before reaction	After reaction
SiO_2	66	69.21	69.15
Al_2O_3	9.5	7.91	7.82
Fe_2O_3	1.1	0.73	0.71
MgO	2	1.71	1.69
Na_2O	0.24	0.14	0.13
K_2O	1.8	0.86	0.85
CaO	3	0.63	0.59
S_{BET} ($m^2 g^{-1}$)	33.28	75.3	41.3
Mesopore specific surface area ^a ($m^2 g^{-1}$)	32.06	72.9	39.8
Total pore volume ($cm^3 g^{-1}$)	0.096	0.169	0.104
Mesopore volume ^b ($cm^3 g^{-1}$)	0.0947	0.141	0.093
Average pore diameter (nm)	10.0981	7.22	8.12

^a and ^b: the mesopore surface area and the mesopore volume were calculated using the BJH method.

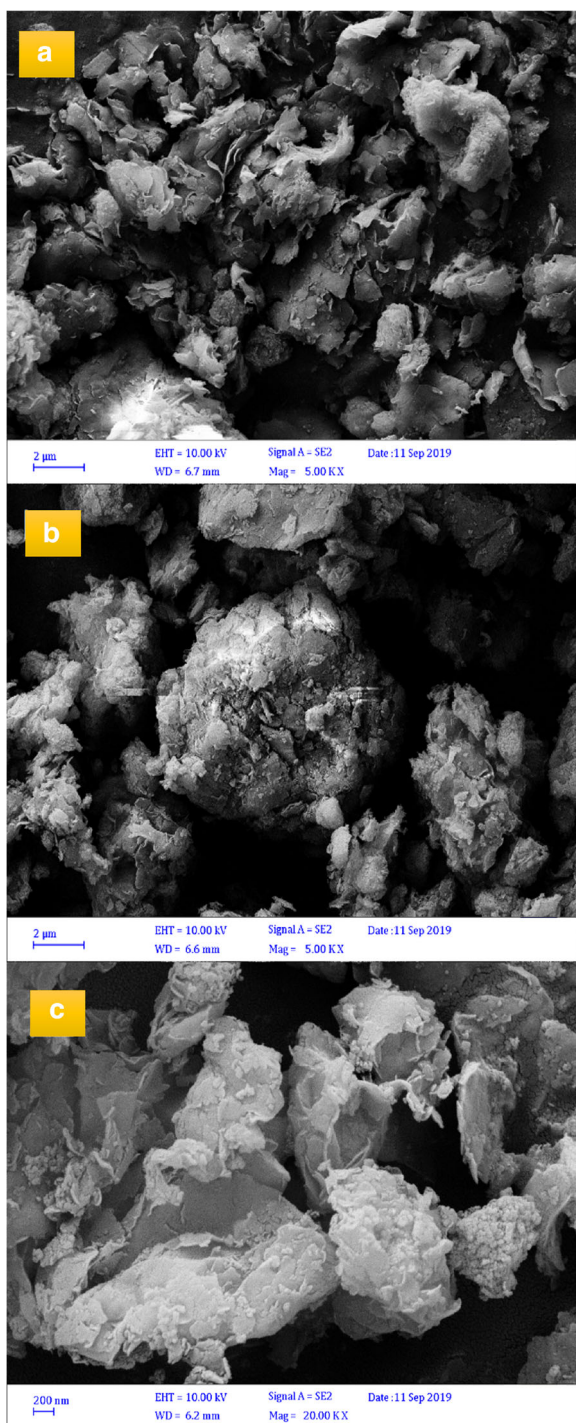


Fig. 10. SEM images of: **a** raw bentonite; **b** and **c** optimum acid-activated bentonite before and after olefin removal reaction, respectively

CONCLUSIONS

In the present study, clay was treated at various acid concentrations and temperatures to prepare a novel and efficient catalyst for the removal of unsaturated hydrocarbons from

aromatic compounds. The results of batch and continuous tests revealed that clay modified with 0.3 M HNO_3 at a temperature of 150°C led to superior activity in comparison with the other samples. The XRD results suggested that the clay modified with 0.3 M HNO_3 affected considerably the crystallinity of Ca-montmorillonite. The XRD patterns showed that the Ca-montmorillonite peak intensity was decreased by HNO_3 activation. The result of TPD analysis indicated that the weak Lewis acid sites played a central role in the catalytic activity, and the sample with many weak Lewis acid sites resulted in better removal of olefins from aromatic compounds. The surface morphology of the modified bentonite indicated that the thermal and acid treatment changed considerably the morphology of the raw bentonite, developing a large number of mesopores. The results of SEM and TPD characterization indicated that the morphology and surface acid sites of the catalyst were stable during the alkylation reaction. The XRD results showed slight changes in the structure of the optimum sample after olefin removal. Finally, potentiometric analysis was employed as an appropriate method to measure the BI of the outlet fluid of both batch and continuous systems.

Compliance with Ethical Statements

Conflict of Interest

The authors declare that they have no conflict of interest.

REFERENCES

- Allothman, Z. A. (2012). A review: Fundamental aspects of silicate mesoporous materials. *Materials*, 5, 2874–2902.
- Alsawalha, M., Roessner, F., Novikova, L., & Bel, L. (2011). Acidity of different Jordanian clays characterized by TPD- NH_3 and MBOH conversion. *International Journal of Chemical and Molecular Engineering*, 5, 570–574.
- Amari, A., Gannouni, H., Khan, M. I., Almesfer, M. K., Elkhaleefa, A. M., & Gannouni, A. (2018). Effect of structure and chemical activation on the adsorption properties of green clay minerals for the removal of cationic dye. *Applied Sciences*, 8, 2302–2320.
- Barrett, E. P., Joyner, L. G., & Halenda, P. P. (1951). The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *Journal of the American Chemical Society*, 73, 373–380.
- Bradley, W. F., & Grim, R. E. (1951). High temperature thermal effects of clay and related materials. *American Mineralogist*, 36, 182–201.
- Centi, G., & Perathoner, S. (2008). Catalysis by layered materials: A review. *Microporous and Mesoporous Materials*, 107, 3–15.
- Chen, C., Wu, W., Zeng, X., Jiang, Z., & Shi, L. (2009). Study on several mesoporous materials catalysts applied to the removal of trace olefins from aromatics and commercial sidestream tests. *Industrial & Engineering Chemistry Research*, 48, 10359–10363.
- Eisenhour, D. D., & Brown, R. K. (2009). Bentonite and its impact on modern life. *Elements*, 5, 83–88.
- Emam, E., Centi, G., Perathoner, S., & Vaccari, A. (2008). Clays as catalysts in petroleum refining industry. *Applied Clay Science*, 3, 161–198.
- Franck, H.-G., & Stadelhofer, J. W. (1988). *Industrial Aromatic Chemistry*. Heidelberg, Berlin: Springer. 460 pp.
- Genuino, H. C., Muizebelt, I., Heeres, A., Schenk, N. J., Winkelman, J. G. M., & Heeres, H. J. (2019). An improved catalytic pyrolysis concept for renewable aromatics from biomass involving a

- recycling strategy for co-produced polycyclic aromatic hydrocarbons. *Green Chemistry*, 21, 3802–3806.
- Guo, H., Zhang, H., Li, Q., Peng, F., Xiong, L., Wang, C., Hu, A., Yao, S., & Chen, X. (2020). Removal of olefins from reforming aromatic hydrocarbons over metal-halide-modified acid-activated Palygorskite. *Energy & Fuels*, 34, 9463–9472.
- Güven, N. (2009). Bentonites – Clays for molecular engineering. *Elements*, 5, 89–92.
- Hao, W., Pudasainee, D., Gupta, R., Kashiwabara, T., Alessi, D. S., & Konhauser, K. O. (2019). Effect of acidic conditions on surface properties and metal binding capacity of clay minerals. *ACS Earth and Space Chemistry*, 3, 2421–2429.
- Klopprogge, J. T. (1998). Synthesis of smectites and porous pillared clay catalysts: a review. *Journal of Porous Materials*, 5, 5–41.
- Kooli, F., Hian, P. C., Weirong, Q., Alshahateet, S. F., & Chen, F. (2006). Effect of the acid-activated clays on the properties of porous clay heterostructures. *Journal of Porous Materials*, 13, 319–324.
- Kumar, P., Jasra, R., & Bhat, T. (1995). Evolution of porosity and surface acidity in montmorillonite clay on acid activation. *Industrial and Engineering Chemistry Research*, 34, 1440–1448.
- Lagaly, G. (2006). Thermally modified clay minerals. Pp. 289–309 in: *Handbook of Clay Science*, 1, Elsevier, Amsterdam.
- Madejová, J., Pentrák, M., Pálková, H., & Komadel, P. (2009). Near-infrared spectroscopy: A powerful tool in studies of acid-treated clay minerals. *Vibrational Spectroscopy*, 49, 211–218.
- Mahmoud, S., Hammoudeh, A., & Al-Noaimi, M. (2003). Pretreatment effects on the catalytic activity of Jordanian bentonite. *Clays and Clay Minerals*, 51, 52–57.
- Marosz, M., Kowalczyk, A., Gil, B., & Chmielarz, L. (2020). Acid-treated clay minerals as catalysts for dehydration of methanol and ethanol. *Clays and Clay Minerals*, 68, 23–37.
- Murilo, F., Luna, T., Cecilia, J. A., Maria, R., & Saboya, A. (2018). Natural and modified montmorillonite clays as catalysts for synthesis of biolubricants. *Materials*, 11, 1764–1781.
- Noyan, H., Önal, M., & Sarikaya, Y. (2007). The effect of sulphuric acid activation on the crystallinity, surface area, porosity, surface acidity, and bleaching power of a bentonite. *Food Chemistry*, 105, 156–163.
- Pu, X., Liu, N. W., Jiang, Z. H., & Shi, L. (2012). Acidic and catalytic properties of modified clay for removing trace olefin from aromatics and its industrial test. *Industrial and Engineering Chemistry Research*, 51, 13891–13896.
- Ross, C., & Shannon, E. (1926). The minerals of bentonite and related clays and their physical properties. *Journal of the American Ceramic Society*, 9, 77–96.
- Roth, W. J., Gil, B., Makowski, W., Marszałek, B., & Eliášová, P. (2016). Layer like porous materials with hierarchical structure. *Chemical Society Reviews*, 45, 3400–3438.
- Salem, A., & Karimi, L. (2009). Physico-chemical variation in bentonite by sulfuric acid activation. *Korean Journal of Chemical Engineering*, 26, 980–984.
- Sulikowski, B. (2006). Nano-structured materials for catalysis. *Catalysis Today*, 114, 125–332.
- Tian, Y., Meng, X., Duan, J., & Shi, L. (2012). A novel application of methanesulfonic acid as catalyst for the alkylation of olefins with aromatics. *Industrial & Engineering Chemistry Research*, 51, 13627–13631.
- Trombetta, M., Busca, G., Lenarda, M., Storaro, L., Ganzerla, R., Piovesan, L., Lopez, A. J., Alcantara-Rodriguez, M., & Rodríguez-Castellón, E. (2000). Solid acid catalysts from clays evaluation of surface acidity of mono- and bi-pillared smectites by FT-IR spectroscopy measurements, NH₃-TPD and catalytic tests. *Applied Catalysis A: General*, 193, 55–69.

(Received 13 June 2020; revised 11 December 2020; AE: William F. Jaynes)