Research paper

Acid activation effect on the catalytic performance of Al-pillared bentonite in alkylation of benzene with olefins

Hossein Faghihian [a],[*], Mohammad Hadi Mohammadi [b]

[a] Department of Chemistry, Shahreza Branch, Islamic Azad University, P.O. Box 311–86145, Shahreza, Isfahan, Iran
[b] Department of Basic Science, Zawul Institute of Higher Education, Post Box 21258, Kabul, Afghanistan

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ABSTRACT

In this research pillared catalysts were prepared by pillaring of bentonite and acid-treated bentonite with aluminum. The synthesized samples were characterized by X-ray diffraction, FT-IR spectroscopy, N_2 adsorption isotherms, NH_3 temperature programmed desorption, scanning electron microscopy (SEM) and elemental and thermal analysis techniques. Acid-treated sample contained lower Al content compared to the untreated sample, but its total pore volumes (TPV) and BET surface area was higher. Alkylation of benzene with linear olefins (1-decene and 1-dodecene) was studied with the prepared catalysts. Acid-activated pillared catalyst, due to its higher surface acidity showed enhanced catalytic activity compared to the untreated sample. The catalysts activity was also enhanced by increasing benzene to olefin molar ratios and reaction temperature. The catalysts showed higher activity when shorter chain hydrocarbon olefin was used. In acid-activated pillared catalysts higher selectivity for 2-phenyl isomer was obtained with 1-dodecene.

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1. Introduction

Alkylation of aromatic hydrocarbons with olefins is an important industrial process for production of linear alkyl benzenes which is the key essential reagent for preparation of synthetic detergents. Alkylation reaction traditionally is catalyzed by aluminum trichloride or hydrofluoric acid. Because of the hazardous nature of the system, there is a need to develop solid acid catalysts to replace the existing production catalyst. Solid acids such as zeolites (Craciun et al., 2007; De Almeida et al., 1994; Yuan et al., 2002), clays (Awate et al., 2004; Borutskii et al., 2007; Guerra et al., 2008), have been studied as alkylation catalysts. By use of acid catalysts, generally high conversions are obtained but the product range is wide. Depending on the properties of catalyst, even with 1-olefins, by branching and double bond isomerization of olefins all mono-alkylated isomers are formed. Other by-products may be formed by poly-alkylation, isomerization and oligomerization of olefins (Craciun et al., 2007). Knowledge of the influence of different experimental parameters on the products range offers an important tool for development of more efficient catalytic processes.

Over the past decade, considerable attentions have been focused on clays as catalyst and catalyst supports because of their porosity, reactivity and thermal stability. Acid-treated montmorillonite was the catalyst commonly used for initial cracking reactions in the 1930s (Thomas and Thomas 1997). Pillared interlayered clays (PILC) were used to optimize the catalytic cracking of crude oil. Catalysts with larger pore size and good hydrothermal stability were suggested to increase the yield of lighter fractions from heavy crude oil (Ding et al., 2001; Frost et al., 1998; Kloprogge, 1998). Katikaneni et al. (1995) used Al-PILC to convert canola oil to fuel using a fixed bed reactor.

Although the clays have shown considerable activity in their raw form, but to improve their activity some chemical and thermal activation steps are needed (Lagaly et al., 2013). PILC prepared with inorganic polycations have high thermal stability, good rigidity, uniform micropores and excellent acidity and provide wide opportunities to be used as solid acid catalysts for variety of organic transformations (Gopal Mishra and Ranga Rao, 2004). The number of ionic precursors and thus the number of pillars introduced in clay depend on the cation exchange capacity (CEC) of the parent clay. Montmorillonite is currently used as a catalyst material because of its relatively high CEC and its potential to modify the interlayer distance by replacing of initial cations. Metals commonly used as ionic precursors are Al, Zr and Ti (Vicente et al., 2013). Aluminum is commonly used as Keggin ion $[(Al_{13}O_4 (OH)_{24} (H_2O)_{12}]^{7+}$ but other mono and polynuclear species may be present depending on the pH of the solution (Benito et al., 1999).

Acid activation of montmorillonite before the pillaring step strongly influences the performance and activity of the clay and produces new material with physicochemical properties intermediate between those of conventional pillared clays and acid-activated clays (Komadel and Madejova, 2013; Vicente et al., 2013). The aim of this work is to

investigate the effect of acid-activation process on the performance of aluminum-pillared bentonite (AlPBent) in alkylation of benzene with long chain [C_{10}, C_{12}] olefins.

2. Experimental

2.1. Techniques

Chemical composition of the samples was determined by XRF method using Bruker S4 PIONEER (Germany) equipment. The CEC of the samples was measured with 0.01 M copper ethylenetetramine solution (Ammann et al., 2005). The crystallinity and structural changes of the samples were examined by X-Ray Diffraction (XRD) technique by a Bruker D8 ADVANCE, P4 PIONEER diffractometer (Germany). FT-IR spectra were prepared by JASCO, FT-IR-6300 spectrometer (Japan) with standard mid-IR DTGS detector. FT-IR spectra were recorded in the range of 400–4000 cm^{-1} with KBr pellets technique. The BET surface area and total pore volume of the catalysts were determined by N_2 adsorption isotherms prepared by BELsorp max 113, Japan, Inc. system.

The micropore volumes ($V\mu$) of the samples were obtained from the t-plot method (Lippens and de Boer, 1965). Temperature programmed desorption (TPD) profile of ammonia was used to evaluate the surface acidity of the samples by a Micromeritics TPD/TPR 2900 instrument equipped with a thermal conductivity detector (TCD). Approximately 0.25 g of the sample was activated under helium flow at 300 °C for 1 h and then ammonia was passed over the sample at 100 °C for 30 min. To remove the adsorbed ammonia, helium was purged to the samples at the same temperature for 1 h. The TPD profiles were obtained from 100 to 550 °C with heating rate of 10 °C min^{-1}. Loss on ignition of the samples was calculated by the thermal curves taken by a Mettler, TG50 Thermal Analyzer from 25 to 900 °C under nitrogen atmosphere. Scanning electron microscopy (SEM) images were prepared by Philips XL SERIES, XL30 (Germany) system to examine the morphology of the samples.

2.2. Chemicals

Bentonite was purchased from Sigma-Aldrich (CAS-No. of 1302-78-9). H_2SO_4 (95–98%), KBr, $CuCl_2$, ethylendiamine, NaOH, aluminum chloride ($AlCl_3$, $6H_2O$, 99%), 1-decene and 1-dodecene were prepared from Merck Company. Benzene (99%) was obtained from Bandar Imam Petrochemical Company (B.I.P.Co.), Iran. All chemicals were research grade and used as received without further purification.

2.3. Synthesis of acid-activated pillared samples

The starting material was sodium bentonite (particle size ≤ 2 μm, CEC of 74 meq/100 g). Two acid-activated samples were prepared by treating bentonite with 2 M and 4 M H_2SO_4 according to the procedure described by Falaras et al. (2000). The samples were designated as A2Bent and A4Bent respectively. Pillared samples were prepared by the method reported by Chae et al. (2001). Appropriate amount of pillaring solutions (aluminum hydroxyl-oligomeric solution, OH/Al molar ratios of 2), required for the Al/clay ratio of 25 (mmol Al/g clay) was added slowly to 1.0 liter of distilled water containing 10 g of the sample (parent and acid-activated bentonite). The final product was dried at 110 °C and calcined at 300 °C. Pillared bentonite was designated as AlPBent and the pillared samples prepared by acid-activated bentonite (A2Bent and A4Bent) were designated as A2-AlPBent and A4-AlPBent respectively.

2.4. Catalytic activity of the samples

The catalytic activity of the synthesized samples was tested in a 100 ml stainless still reactor containing 0.3 g of calcined catalysts. The molar ratios of the reactant and the temperature were adjusted and the mixture was stirred for 270 min. Alkylation products were analyzed by FISONS GC 8000 series gas chromatograph with a DB-17 capillary column coupled to a flame ionization detector.

3. Results and discussion

3.1. Catalyst characterization

Bentonite has many industrial applications and montmorillonite is its principal constituent. It has interlayered cations with weak bonds. These cations are easily exchangeable, causing swelling of the structure. As a result, the opening of the layer permits exchange of the existing cations with bigger cations, such as polyhydroxications (Sapag and Mendioroz, 2001). The chemical composition of the bentonite obtained by XRF method revealed that the framework cations were mainly Al^{3+}, Fe^{3+} and Mg^{2+} and Na^+, K^+ and Ca^{2+} were exchangeable interlayer cations (Table 1). The effect of acid-activation on the structural and textural modification was studied by different techniques including chemical analysis, XRD, FT-IR, SEM, CEC and surface area measurements.

By acid-treatment, the interlayer cations were replaced by H^+ ions followed by dissolution of octahedral aluminum and subsequent dissolution of the structural cations. Tetrahedral silica of the structure was not dissolved at low acid concentration, while the octahedral layer

Table 1
Physicochemical properties of samples.

Catalyst	Concentration (mass%)					
	Bentonite	AlPBent	A2Bent	A4Bent	A2-AlPBent	A4-AlPBent
SiO_2	58.27	54.32	60.3	61.67	56.98	56.12
Al_2O_3	20.53	25.12	18.66	18.23	23.24	24.09
Fe_2O_3	3.75	3.45	3.34	3.26	3.03	3.12
MgO	2.24	1.78	1.67	1.65	1.45	1.55
Na_2O	2.10	0.22	0.23	0.28	0.20	0.20
CaO	1.37	0.18	0.47	0.23	0.08	0.08
K_2O	0.38	0.26	0.32	0.33	0.29	0.29
LOI[a]	10.24	14.51	14.48	13.97	14.36	14.13
CEC[b] (meq/100 g)	74.73	21.18	68.21	67.47	23.01	20.15
S_{BET} (m^2/g)	34	265	129	127	296	278
TPV[c] (cm^3/g)	0.123	0.198	0.270	0.269	0.298	0.299
V_μ[d] (cm^3/g)	–	0.112	–	–	0.155	0.135
d[e] $_{(001)}$ (Å)	11.86	18.69	12.27	11.78	18.21	18.31
Acidity (meq NH_3/g)	0.04	0.68	0.78	0.87	0.96	1.42

[a]Loss on Ignition determined by DTG method, [b]Measured by adsorption of cupper ethylenetetramine. [c]Total pore volume at a relative pressure of 0.99. [d] Micropore volume obtained from the t-plot method, [b]Basal spacing obtained by XRD.
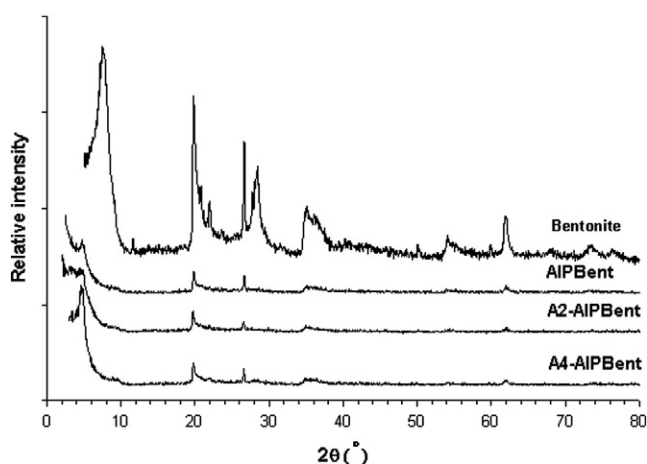
Fig. 1. XRD pattern of Bentonite, AlPBent, A2-AlPBent and A4-AlPBent.

was affected at this condition. Therefore, the increase in the silica content of the sample treated with 2 M H_2SO_4 was attributed to the dissolution of octahedral aluminum and the exchangeable cations (Tyagi et al., 2006). By increasing acid concentration more exchangeable cations were replaced by H^+ ions (Table 1).

CEC of untreated bentonite (74.73 meq/100 g) decreased to 68.21 and 67.47 meq/100 g respectively in A2Bent and A4Bent samples. The decrease in CEC was attributed to the dissolution of octahedral cations and protonation of the SiO groups. The significant decrease in the CEC of AlPBent sample (21.18 meq/100 g) indicated that the exchangeable cations were substituted by Al during the pillaring process. Similar substitution was occurred in A2-AlPBent and A4-AlPBent samples, and the CEC values were decreased to 23.01 and 20.15 meq/100 g respectively (Table 1). Metal polyoxycations as intercalated species were converted into the corresponding metal oxide clusters after heating at elevated temperatures. Formation of metal oxide was incomplete at temperature below 500 °C. The oxide was rigid enough to prevent the interlayer spaces from collapsing, and to generate micropores larger than those of the conventional zeolites. The fixed cations were not accessible for

other ions to exchange (Chae et al., 2001; Gopal Mishra and Ranga Rao, 2004).

Thermal curves of the samples taken between 25–900 °C showed similar mass loss behavior (Figures are not shown). The mass loss occurred between 50 and 200 °C was attributed to the removal of physically adsorbed water. The second mass loss at 550–700 °C was assigned to the removal of water molecules coordinated to the pillars and also dehydroxylation of the pillars.

Seven diffraction lines at 2θ of 7°, 20°, 22°, 27°, 35°, 54° and 62° were observed in the XRD pattern of the parent bentonite (Fig. 1). The lines at 2θ of 22° and 27° belonged to cristobalite and quarts impurities respectively. It was deduced that acid activation did not dramatically change the structure of the mineral but partial de-alumination of the samples caused significant decrease in the lines intensities (Jozefaciuk and Bowanko, 2002; Snall and Liljefors, 2000).

After acid-treatment and pillaring process, the (001) lines at 2θ = 7° shifted towards lower degree, showing enlargement of the basal spacing of the clay (Table 1). The basal spacing of A2-AlPBent and A4-AlPBent samples were similar to that of AlPBent sample but the basal reflection had higher intensity. Higher quantities of pillars changed the ordering of the layers in c-direction and consequently increased the basal reflection.

In the FTIR spectra of the parent and synthesized samples (Fig. 2), the bands at 1045 and 526 cm^{-1} were attributed to Si-O in-plane stretching and Si-O bending vibrations respectively. The shoulder at 1115 cm^{-1} showed the Si-O out-of-plane stretching vibration. The broad band at 3438 cm^{-1} belonged to the stretching vibration of the hydroxyl groups of water molecules. The band at 3623 cm^{-1} was assigned to hydroxyl groups coordinated to octahedral cations (Madejova et al., 1998) (Fig. 2A). The presence of three bending vibrations of hydroxyl groups (AlAlOH at 920 cm^{-1}, AlFeOH at 885 cm^{-1} and AlMgOH at 845 cm^{-1}) indicated that Al^{3+} was substituted by Fe^{2+} or Mg^{2+} in octahedral layer. Furthermore, the band at 793 cm^{-1} and the shoulder around 1115 cm^{-1} reflected the presence of cristobalite. The shoulder near 620 cm^{-1} was attributed to the Al–O–R (R = Al and Mg) vibration of octahedral atoms (Fernandes et al., 2007). The band at 692 cm^{-1} confirmed the presence of quartz which previously was detected by XRD (Tyagi et al., 2006).
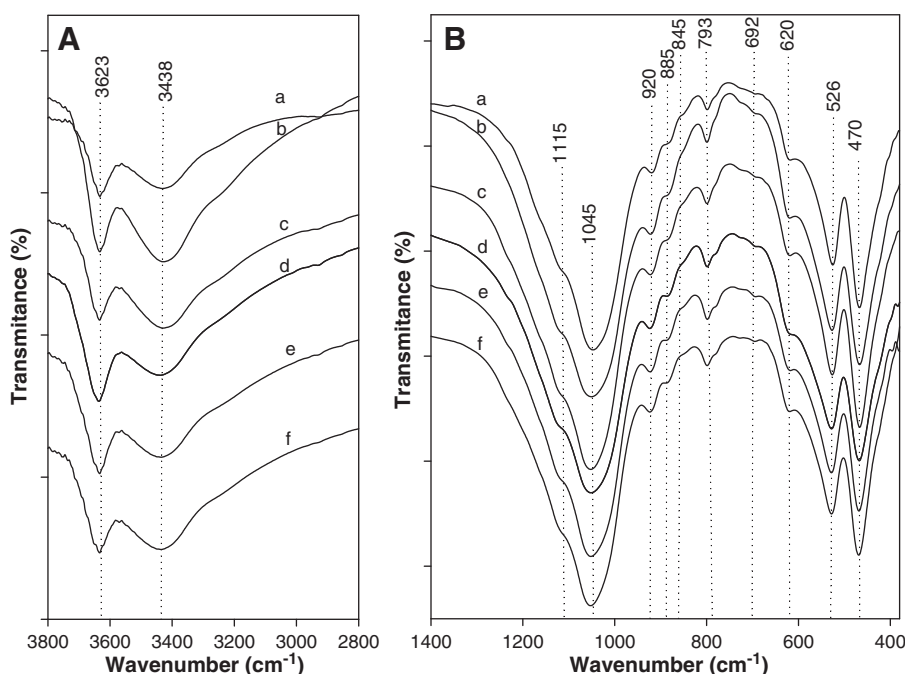

Fig. 2. FTIR spectra of the samples: Bentonite (A), A2Bent (B), A4Bent (C), AlPBent (D), A2-AlPBent (E), A4-AlPBent (F).
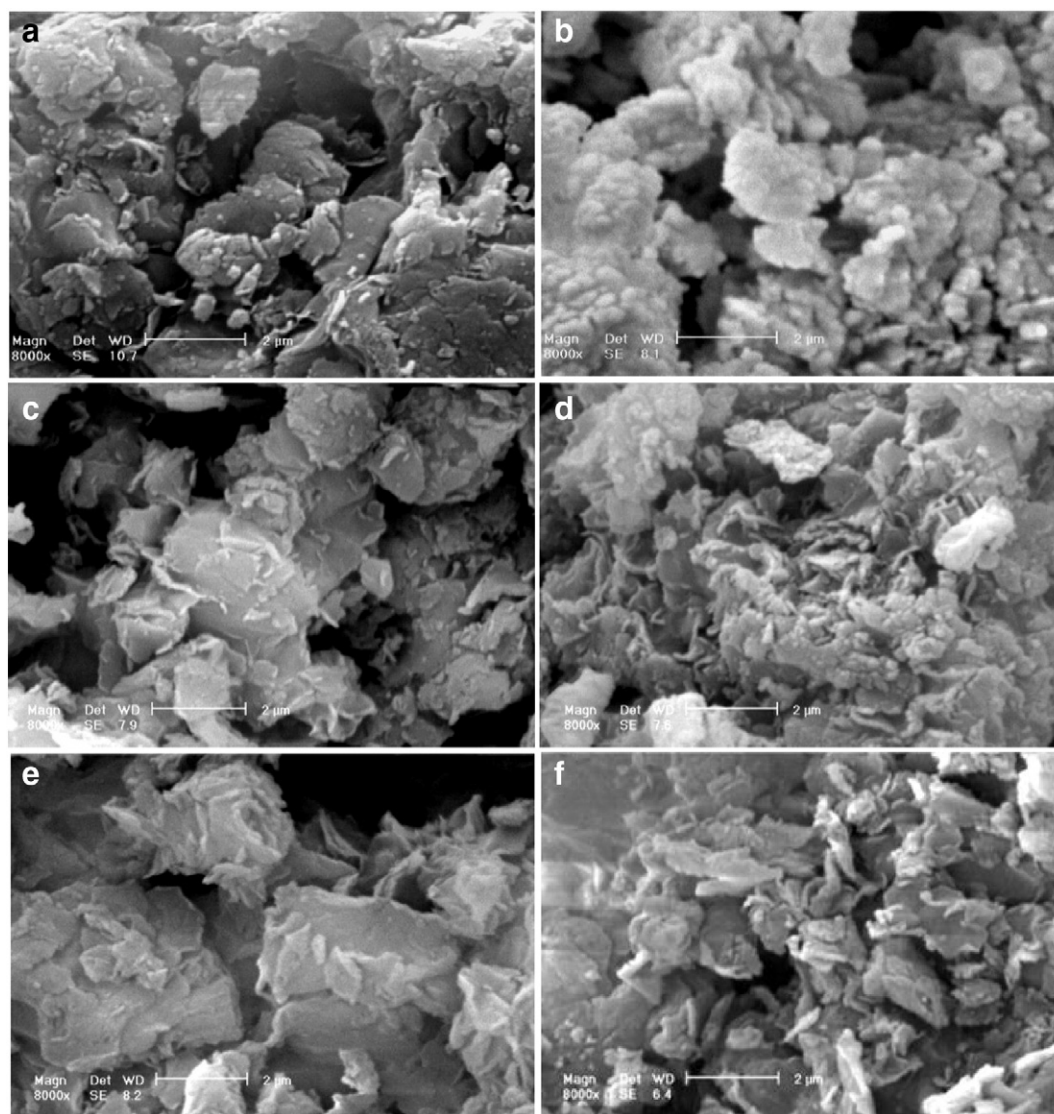
Fig. 3. SEM micrograph of the samples: Bentonite (a), AlPBent (b), A2Bent (c), A4Bent (d), A2-AlPBent (e), A4-AlPBent (f).
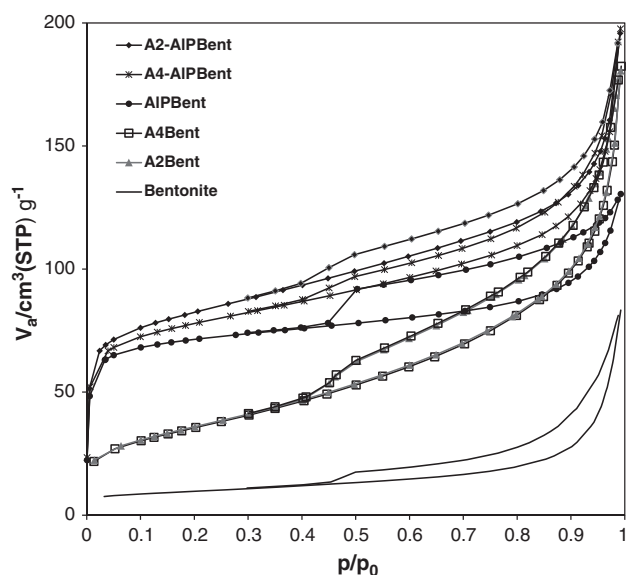

Fig. 4. Nitrogen adsorption-desorption isotherms.

In the FTIR spectra of the acid-activated samples the position and shape of the band are slightly changed. The band at 1045 cm^{-1} was shifted to higher wavenumbers (Fig. 2B) and the intensity of hydroxyl bending vibration at 845 cm^{-1} (Al-Mg-OH) and 885 cm^{-1} (Al-Fe-OH) was reduced (Tyagi et al., 2006).The decrease in the intensities of the bands was related to the decrease of Mg^{2+} and Fe^{2+} content and in agreement with chemical analysis data (Table 1). The bands at 793 cm^{-1} belonged to cristobalite was shifted to 796 cm^{-1} and its intensity was increased after acid treatment. The intensity of the band

Table 2
Conversion of alkylation reaction at different benzene to olefin molar ratio. Conditions: temperature, 145 °C; catalyst mass, 0.3 g (1% of total reaction mixture); reaction time, 4.5 h.

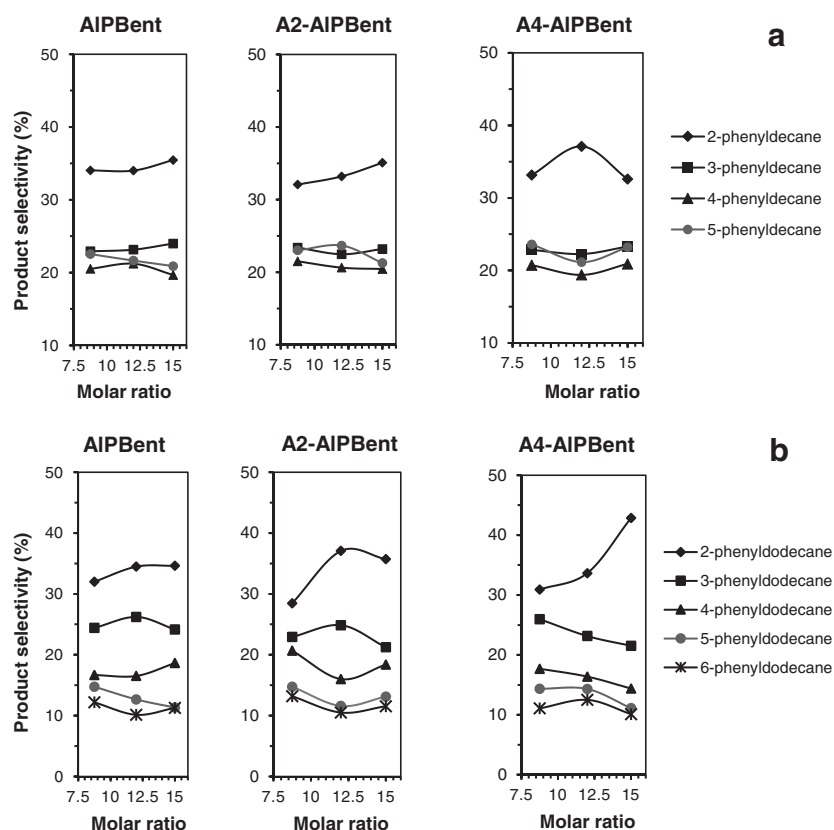| Bz:Olefin ratio	8.75:1	12:1	15:01
1-decene			
AlPBent	83.80	93.97	>98
A2-AlPBent	94.11	>98	>98
A4-AlPBent	91.80	>98	>98
1-dodecene			
AlPBent	20.62	21.52	23.47
A2-AlPBent	28.15	30.70	32.14
A4-AlPBent	25.35	25.97	29.81

Fig. 5. Effect of molar ratio on product selectivity in alkylation of benzene with 1-decene (a) and 1-dodecene (b). Conditions: temperature, 145 °C; catalyst mass, 0.3 g (1% of total reaction mixture); reaction time, 4.5 h.

at 692 cm^{-1} belonged to quartz was also increased after acid treatment. This was in agreement with the results of chemical analysis which showed higher SiO$_2$ content for A2Bent and A4Bent after acid treatment (Table 1).

By pillaring, the band at 3438 cm^{-1} was broadened which was attributed to the introduction of the OH groups of the pillars and was interpreted as the effect of pillaring (Kurian and Sugunan, 2003). The increase in the intensity of the band at 3438 cm^{-1} was related to the presence of aluminum oxocations in the samples.

In A2-AlPBent and A4-AlPBent asymmetric stretching vibrations of SiO$_2$ tetrahedra were shifted to 1060 cm^{-1}. This was caused by acid treatment of the sample before pillaring. This shift was not observed in AlPBent. The FTIR spectrum of the treated samples was basically similar to the parent clay indicating that acid and pillaring treatments did not change the structure of the starting material.

The SEM images of the samples shown in Fig. 3 revealed that bentonite consisted of thick particles with irregular shape and partly a mass of

Table 3
Effect of temperature on the catalytic activity and 2-phenylalkane selectivity. Conditions: catalyst mass, 0.3 g (1% of total reaction mixture); benzene to olefin molar ratio, 12:1; reaction time, 4.5 h.

Temperature	115 °C		130 °C		145 °C	
	Conv. (%)	Select. (%)	Conv. (%)	Select. (%)	Conv. (%)	Select.(%)
Bz:1-decene (12:1)						
AlPBent	52.27	37.19	91.22	42.46	93.97	34.01
A2-AlPBent	55.56	35.10	94.17	41.31	>98	33.21
A4-AlPBent	60.11	32.84	97.27	55.14	>98	37.10
Bz:1-dodecene (12:1)						
AlPBent	20.98	31.23	21.23	35.61	21.52	34.48
A2-AlPBent	28.13	30.41	29.64	34.01	30.70	37.06
A4-AlPBent	25.14	31.82	25.34	34.52	25.97	33.64

flake shape (Fig. 3a). In AlPBent sample some mass of flake were disappeared and due to the changes occurred in the interlayer sections some of the particles were agglomerated (Fig. 3b). After acid-treatment the particles became smaller and thinner but the lamellar structure of the bentonite was remained (Fig. 3c for A2Bent) and (Fig. 3d for A4Bent). In A2-AlPBent (Fig. 3e) and A4-AlPBent (Fig. 3f) samples, leaf like agglomerates were appeared. The morphology changes indicated that some Al$_{13}^{7+}$ ions entered the interlayer space of acid-activated samples.

Nitrogen adsorption-desorption isotherms of the samples are shown in Fig. 4. According to the IUPAC classification the isotherms were of IV type with a well defined H4 hysteresis loop denoting a slit-shaped porosity between plate-like particles. H4 hysteresis loops are generally observed with complex materials containing both micropores and mesopores (Sing et al., 1985).

By acid treatment, the cations were leached out and replaced by hydrogen ions and the edges of the platelets became more opened. It was clear from the figure that by pillaring, an increase in the surface area was obtained, and that the pillared material kept the layered structure of the initial clay. Acid-activation significantly increased the surface area and total pore volume (Table 1). It was suggested that accessibility of the active sites to the chemical reagents was improved by acid treatment.

Acidity of the systems, measured by TPD of ammonia is shown in Table 1. The number of acid sites of the samples was enhanced by acid treatment and pillaring process. The enhancement in acid-activated pillared samples was higher than the untreated pillared bentonite and the maximal value was obtained in pillared sample activated with 4 M H$_2$SO$_4$.

3.2. Activity of the catalysts

The catalytic activity of the samples was examined in alkylation of benzene with 1-decene and 1-dodecene. The alkylation of benzene

with olefins proceeded through the carbenium ion mechanism. For 1-decene and 1-dodecene, formation of five or six carbenium ions of the olefin was possible. Carbenium ions with higher C-number are more stable. 1-phenyldecane and 1-phenyldodecane were the least stable isomers. In fact, formation of 1-phenylalkane has not been reported for homogeneous and heterogeneous catalysts, and 2-phenylalkane was the first reported stable isomer. The isomeric distribution of the products was related to the shape selectivity and the acidity of the catalysts. Thus, the secondary carbon atom of the alkyl chain was first attached to benzene, and further products were formed by the proton shifts caused by the catalyst. After monoalkylation, under a certain set of conditions such as high concentration of olefin and reaction temperature, dialkylated product was formed. The amount of dialkylated product was reduced by using excess molar of benzene over olefin and by controlling the temperature, acidity and the amount of catalyst loading. In this research, the effect of different parameters including temperature, benzene to olefin molar ratio and amount of catalysts were evaluated. The conversion of the reaction was calculated based on olefin consumption and the selectivity of the reaction was obtained by calculating the percentage of n-phenylalkane products (Craciun et al., 2007). For industrial application high selectivity to the linear 2-phenyl isomer was the major target as this isomer yields detergents with better emulsifying properties and better biodegradability (Cohen et al., 1995).

3.3. Effect of molar ratio

The catalytic activity of the catalysts was investigated at different molar ratios of benzene to olefin (8.75, 12 and 15) at 145 °C (Table 2). The alkylation products of benzene with 1-decene were n-phenyldecane isomers. Dialkylated products and olefin oligomers were not detected. An excess of benzene only favored the formation of monoalkylated derivatives. For the pillared catalyst, even with benzene to olefin molar ratio of 8.75:1 (industrial ratio) the conversion of 91.80% was obtained. With higher benzene to 1-decene molar ratio, the conversions higher than 98% was obtained. At the benzene/olefin ratio of 8.75:1, the A2-AlPBent catalyst despite its lower total surface acidity showed higher activity compared to A4-AlPBent. This was explained by higher surface area of A2-AlPBent sample that improved accessibility of active sites (Table 1). In higher benzene: olefin ratios the effect of surface area became less significant and the activity increased by increasing of total surface acidity. Comparison of acid-activated pillared samples to the conventional pillared samples indicated that the acid treatment prior to pillaring process enhanced the activity of the catalyst even at benzene: 1-decene ratio of 8.75 and 12. This was in agreement with the acidity sites and surface area of the samples. The A2-AlPBent and A4-AlPBent samples had much larger surface area than the parent clay resulting to an increase in the number of the acid sites and also an improved accessibility of the active sites to the reactants compare to the untreated pillared clay. Conversion of 93.4% of 1-decene by AlPBent was in agreement with the data reported by Perego and Ingallina (2002), while the conversions by A2-AlPBent and A4-AlPBent were higher. The conversion of 1-decene obtained by acid-activated Al-pillared samples was also greater the value reported for Zr-pillared clay (Awate et al., 2004; Guerra et al., 2008).

In alkylation of benzene with 1-dodecene lower activity was observed. This can be explained by restriction to accessibility of longer

olefins chain. The products of reaction were 2-phenyldodecane, and other linear isomers. Dialkylated product and olefin oligomers were not detected. Conversion increased by increasing the benzene to 1-dodecene molar ratio. At the equilibration of the reversible reaction, increasing the amount of benzene increased the olefin conversion (Thomas et al., 2006). Higher catalytic activity of A2-AlPBent compared to other samples (Table 2) reflected the higher surface area of the catalyst and more accessibility of the active sites due to less space restriction for 1-dodecene. AlPBent showed lower conversion in both molar ratios because of its lower acidity and surface area.

The effect of molar ratio on product selectivity is shown in Fig. 5. All samples showed good shape selectivity for 2-phenyldecane isomer, whereas the maximal selectivity for 2-phenyldecane (37.10%) was obtained at 12:1 molar ratio by A4-AlPBent sample (Fig. 5a).

The catalysts showed higher shape selectivity for 2-phenyldodecane compared to 2-phenyldecane. The acid-activated pillared samples showed higher selectivity for 2-phenyldodecane than AlPBent. The maximal selectivity (42.86%) at molar ratio of 15:1 was obtained by A4-AlPBent (Fig. 5b).

3.4. Effect of temperature

The effect of temperature on conversion and selectivity of alkylation process was studied at 115, 130 and 145 °C (Table 3). Since the olefin conversion for both molar ratios of 15:1 and 12:1 was similar, the lower ratio was selected for the experiments. The maximal selectivity for 2-phenyldecane was obtained at 130 °C (41.3% and 55.1% respectively for A2-AlPBent and A4-AlPBent samples). The Lower selectivity obtained at 145 °C was attributed to the rapid equilibration of the olefin isomer and fast diffusion of the bulkiest linear alkylbenzene isomer out of the catalyst cavities (Thomas et al., 2006). The low activity of the catalysts for 1-dodecene was attributed to the limited access of longer chain 1-dodecene to the active sites of the catalysts. The activity of acid-activated pillared sample was better than AlPBent in both temperatures. The maximal conversion of 30.70% was obtained for A2-AlPBent at 145 °C. At this temperature 1-dodecene can conquest the restriction of accessibility because of the higher surface area of the catalyst. It was found that no dialkylated product was formed when the temperature was increased from 115 to 145 °C. This was attributed to the presence of excess benzene in the reaction mixture. Generally, it can be concluded that the temperature has positive influence on alkylation of benzene with 1-decene and 1-dodecene.

3.5. Effect of catalyst amount

To examine the effect of catalyst amount, the reaction was conducted by changing the A2-AlPBent catalyst loading in the range of 0.25–1.75 mass% and keeping benzene to 1-decene molar ratio of 8.75 (within industrial process ranges) at optimized temperature of 145 °C (Table 4). The conversion increased from 79.9% to 94.1% by increasing catalyst mass from 0.1 to 0.3 g and then remained almost constant. The constant conversion after 0.3 g catalyst loading was attributed to the deficiency of the reactant molecules. The value (0.3 g = 1 mass%) was selected as the optimized catalyst amount. The selectivity for 2-phenyldecane was not significantly changed with increasing of catalyst mass. Optimized catalyst loading for alkylation of benzene with

Table 4
Effect of catalyst mass, Conditions: catalyst, A2-AlPBent; temperature, 145 °C; benzene to olefin molar ratio of 8.75; reaction time, 4.5 h.

Mass of catalyst (g)	1-decene conversion (%)	2-phenyldecane selectivity (%)	1-dodecene conversion (%)	2-phenyldodecane selectivity (%)
0.1	79.94	32.11	22.41	28.38
0.2	82.21	32.14	26.34	28.15
0.3	94.11	32.08	28.13	28.47
0.4	94.07	32.10	27.49	27.98
0.5	94.10	32.13	27.91	26.84

Table 5
Regeneration of catalyst. Conditions: catalyst amount, 1mass %; benzene to 1-decene molar ratio, 12; temperature, 145 °C; reaction time, 4.5 h.

Cycle	A2-AlPBent		A4-AlPBent	
	Conv. (%)	2-φ select. (%)	Conv. (%)	2-φ select. (%)
One (fresh)	>98	33.21	>98	37.1
Two	>98	33.06	>98	38.11
Three	97.42	34.11	97.82	37.23

1-dodecene was similar to the value obtained for 1-decene (0.3 g) (Table 4).

3.6. Regeneration of the catalyst

To examine the catalytic activity of the regenerated catalysts, the used A2-AlPBent and A4-AlPBent samples were separated by filtration and washed with hot benzene. To remove the reaction-mixture components, the sample was gradually heated (heating rate of 10 °C/min, under nitrogen flow) to 200 °C and maintained for 2 h at this temperature. The catalysts were then activated at 500 °C for 3 h in air flow. The activated catalysts were reused for alkylation of benzene with 1-decene at optimized reaction conditions. The procedure was repeated for three cycles. The result showed that no significant decrease in the catalytic activity and product selectivity was of the catalyst observed (Table 5).

4. Conclusion

The XRD patterns of the samples showed that by acid treatment and pillaring process no major change was observed on the structure of bentonite. The results of BET and TPD studies showed that the specific surface area and acidic sites of the acid-treated samples were significantly higher than those of un-treated sample. The pillared acid-activated catalyst had basal spacing and specific surface area comparable to the conventional pillared clays with significantly higher pore volume and acidity. The higher acidity of acid-treated samples compared to the conventional pillared clays was attributed to the higher acid sites produced on the clay matrix. The alkylation of benzene with 1-decene and 1-dodecene by A2-AlPBent, A4-AlPBent and AlPBent catalysts showed that the acid-activated pillared catalysts had more activity than AlPBent. In these catalysts the conversion was greater than the value reported for Zr-PILC. Among the studied catalyst, the acid-activated pillared catalysts showed the highest catalytic activity (of the total reaction mixture). Under the optimized reaction conditions (145 °C, benzene: 1-decene molar ratio of 12 and 1 mass% catalyst concentration) A2-AlPBent and A4-AlPBent showed full conversion of 1-decene and higher shape selectivity of 33.21 % and 37.10 % respectively. The results showed that the catalysts activity was higher with the shorter olefin chain. The acid-treated samples also showed greater selectivity for 2-phenylalkane isomer compared to the untreated samples. A2-AlPBent catalyst showed highest conversion (32.14%) of 1-dodecene under reaction condition (145 °C, benzene to 1-dodecene molar ratio of 12, and time 4.5 h). The 2-phenyldodecane selectivity of 35.71% was also obtained. Dialkylated product and olefin oligomer were not observed under the prevailing experimental conditions and the catalyst exhibited a full selectivity towards linear alkylbenzene. Acid-activated pillared catalysts were recyclable, environmental friendly and can be used in similar catalytic reactions.

Acknowledgments

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