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Characterization of AlFe-Pillared Unye bentonite: A Study of the surface acidity and catalytic property

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Abstract

Aluminium-iron-pillared bentonite has been prepared by incorporation of the iron mixed aluminium-polyoxocation into bentonite layers and characterized by the powder X-Ray diffraction, Fourier transform infrared, thermal analysis and surface area measurement techniques. The characteristic d₀₀₁ basal spacing of raw bentonite increased with the pillaring process and reached to 18.05 Å. The siloxane layers of bentonite were perturbed and the positions of Si-O stretching vibrations were altered by pillaring process. However, these pillars in the interlayer gallery spacing enhanced the thermal stability of bentonite. The new micropores were formed by the pillaring process and the specific surface area of raw bentonite increased by ca. 2-fold for aluminium-iron-pillared bentonite. FTIR spectra and thermal analysis curves of pyridine adsorbed samples clearly show that the surface Lewis acidity of aluminium-iron-pillared bentonite is greater than that of raw bentonite. Raw and aluminium-iron-pillared bentonites have been utilized as solid catalysts for benzoylation of benzene with benzoyl chloride. The aluminium-iron-pillared bentonite catalyst showed promising catalytic activity whereas raw bentonite showed no catalytic activity in benzoylation of benzene with benzoyl chloride.

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1. Introduction

Clays have been used as adsorbents, ion exchangers and catalysts in many fields of industry because of their environmental compatibility, lower cost, operation simplicity, easy availability and reusability [1-6]. However, the weak porosities, low acidities and thermal stabilities of raw clays limit their further potential applications in various industries. Therefore, the pillaring process, which leads to the formation of a new class of material known as pillared clays, is a commonly used process for modifying the structural, thermal and surface properties of layered clays such as smectites [7-10]. Pillared clays are prepared by the insertion of various polyoxocations into clay layers with the replacement of exchangeable cations, followed by calcinations. The calcinations induce the dehydration and dehydroxylation of polyoxocations and thus yield thermally stable oxides, known as pillars, which act as pillar to prop up the opened clay layers and prevent their collapse [11-13]. Changing the type of pillars influences the textural, structural, catalytic and adsorptive properties of pillared clays directly and for this reason, many different pillared clays are prepared by forming metal oxides and, mixed metal oxides into the clay layers such as Al₂O₃, ZrO₂, TiO₂, Cr₂O₃, Fe₂O₃, Al₂O₃-ZrO₂, Al₂O₃-SiO₂, Al₂O₃-Fe₂O₃, Al₂O₃-MoO₃, Al₂O₃-La₂O₃, Al₂O₃-V₂O₃ etc [14-24]. Pillared clays which have good thermal stability, high surface area, suitable porosity, shape selectivity and enhanced acidities (both Brønsted and Lewis acidic sites) are potential heterogeneous catalyst for organic reaction such as cracking, oligomerization, oxidation, acetalization, isomerisation, alkylation of aromatic hydrocarbons, methanol conversion, decomposition of organic pollutants etc [25-32]. The conversion and the selectivity of these reactions depend on the concentration, type and strength of the acid sites [33]. Hammet indicator method, n-butylamine back titration, FTIR analysis of the adsorbed probe molecules and thermal decomposition of probe base molecules from catalyst surface are used for rapid determination of the type and amount of acid sites in solid catalyst [34-36].

Furthermore, Friedel-Crafts alkylations and acylations are most common test reactions used for examining the acidic properties of catalysts [37-42]. These reactions are executed by utilizing various homogeneous Lewis acid catalysts such as AlCl₃, HF, ZnCl₂, FeCl₃ or BF₃ but these homogeneous catalysts originate some problems, including corrosion, toxicity, separation difficulties, recovery from the reaction product, disposal of wastes and catalysts [43-44]. Clays and modified clays are particularly promising candidates to replace liquid acids in Friedel Crafts reactions and other chemical reactions due to their superior properties

such as eco-friendly nature, non-toxicity, simple filtration, non corrosive form and reusability [15,37-42].

In the present study, the structural and thermal properties of raw Unye bentonite and Fe-Al-pillared bentonite was examined by using the powder X-Ray diffraction (PXRD), Fourier transform infrared (FTIR), thermal analysis (TG-DTG) and surface area measurement techniques. The surface acidity and type of acidic sites in bentonites were determined by FTIR and thermal decomposition measurements with the use of pyridine as a probe molecule. The benzoylation of benzene with benzoyl chloride was utilized as a model reaction to investigate acidic manner and catalytic activities of raw and pillared bentonites.

2. Experimental

2.1. Materials

The clay used as the starting material in the preparation of AlFe-PILC sample was Unye bentonite from Turkey. The raw bentonite (RB) dried at 105 °C was mixed with 100 ml of 0.1 M NaCl solution at room temperature for 1 day. The products (Na-B) were washed with deionized water thoroughly and AgNO₃ test was applied to the filtrate. The solid products which were dried at 105 °C were ground to 200 μ m.

2.2. The preparation of the materials

The pillaring reagent was prepared by slow addition of 0.2M NaOH solution to 0.2M a mixture of Al(NO₃)₃ and Fe(NO₃)₃ (Al/Fe= 9/1) solution to reach an OH/(Al+Fe) molar ratio of 2.2. The pillaring solution was aged for 12 days at room temperature under constant stirring to allow the formation of the iron mixed aluminium polyoxycation. The pillaring solution is added drop wise to a 2% suspension of the Na-B in the ratio of 10 mmol of metals (Al+Fe) per gram of clay. The suspension was aged for 7 days at 40 °C, then it was filtered off and the supernatants were washed with deionized water until the conductivity was reduced to below 10 μ S. Finally, the solid products were calcined at 400 °C for 4h and AlFe-PILC-B sample was obtained.

The bentonite samples were dried in hot air oven for 24 h at 120 °C before pyridine treatment. Exposure of RB and AlFe-PILC-B surfaces to pyridine (Py) were carried out by heating 0.01g samples with 1ml pyridine (bp=115°C) in sample cup at 120°C for 1h in the oven [36].

After cooling down to room temperature and adsorption of pyridine, the sample adsorbed pyridine was evacuated for 20 min at several temperatures (120-320 °C). The chemisorped pyridine onto RB and AlFe-PILC-B samples were labelled as RB-Py and AlFe-PILC-B-Py, respectively.

2.3. Catalytic experiment

The benzoylation of benzene with benzoyl chloride has been selected as the test reaction to investigate surface acidity and catalytic properties of raw and AlFe-PIL-B. To a mixture of benzoyl chloride (1 mmol, 116 μ L) and benzene (4 mL) was added 400 mg of catalyst. The reaction mixture was then heated to 80 °C and stirred for 24 h [40,41]. After evaporation of benzene under reduced pressure (10 mbar, 25 °C) the residue was diluted with saturated NaHCO₃ (10 mL) and extracted with dichloromethane (3x15 mL). The solvent was evaporated and the product was purified by silica gel column by eluting with EtOAc-hexane (02:98) to give benzophenone as the white powder (65 mg, 46%). ¹H-NMR (200 MHz, CDCl₃, ppm) δ 7.83-7.78 (m, 4H), 7.62-7.43 (m, 6H); ¹³C-NMR (50 MHz, CDCl₃, ppm) δ 198.6, 139.6, 134.3, 132.0, 130.2; IR (KBr, cm⁻¹) 3059, 1658, 1598, 1577, 1446, 1317, 1277, 1176, 1149, 941, 919.

The XRPD patterns were obtained at ambient temperatures on a Rigaku 2000 automated diffractometer by using Ni filtered CuK_{α} radiation (λ =1.54050 Å; 40kV and 40mA). Bragg's law, defined as $n\lambda = 2dSin\theta$, was used to compute the crystallographic spacing (d) for the examined bentonite samples. The FTIR spectra of the bentonite samples were recorded on a Bruker Vertex 80V-spectrometer equipped with a MCT/A detector in the region 4000-400 cm⁻¹ at a resolution of 4 cm⁻¹, using KBr pellet technique. Specimens for measurement were prepared by mixing 0.9 mg of the sample powder with 70 mg of KBr and pressing the mixture into a pellet. The TG and DTA curves were scanned by using a PYRIS Diamond TG/DTG apparatus in a dynamic air atmosphere (heating rate: 10 °C min⁻¹, platinum crucibles, mass ~10 mg and temperature range 30-1000 °C). Nitrogen adsorption/desorption isotherms were measured at 77K (-196°C) with a Quantachrome Autosorb-İQ analyzer. The samples were degassed in vacuum at 275 °C for 6h prior to the textural measurements at 77K (-196°C). Specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) method adsorption data in the relative pressure (P/Po) range 0.02-1.00. The micropore surface area and micropore volume were calculated by t-plot analysis. The pore size distributions were derived from adsorption branches of isotherms applying the non-local density functional theory (NLDFT) method for cylindrical pores.

3. Results and discussion

3.1. PXRD data of samples

Fig. 1. shows the PXRD patterns of the RB and AlFe-PILC-B samples. The d_{001} , d_{020} -100, $d_{130-200}$ and d_{060} reflections of the main montmorillonite component were observed at 5.59, 19.75, 35.05 and $61.83(2\theta)$ with the corresponding distance of 15.80, 4.49, 2.56 and 1.50 Å, respectively (Fig. 1a). The high CaO content (1.25%) and the basal spacing of RB (d_{001} = 15.80 Å) indicate that bentonite contains a calcium-montmorillonite as a dominant clay mineral [45,46]. In addition, the d_{060} peak value of 1.50 Å indicates the presence of an Al-rich dioctahedral montmorilonite. The bands originating from external clay component cristobalite are observed at 21.65, 28.11 and 49.01(2 θ) with the distance of 4.10, 3.17 and 1.86 Å, respectively. It may be concluded from the comparison of the intensities of the d_{001} peak of RB and the diffraction of the nonclay component that the main component of bentonite is montmorillonite. When the RB interacts with pillaring solutions, an expansion is observed along the c-axis. The characteristic d_{001} spacing of raw bentonite increased from 15.80 to 18.05 Å for AlFe-PILC-B which denote the formation of the (FeAl)₂O₃ pillars species into the interlayer space of bentonite after calcinations. This result is in agreement with the previous literature [8,10,19,21] (Fig. 1b). Furthermore, the diffraction peaks belonging to the $d_{020-100}$, $d_{130-200}$ and d_{060} planes of bentonite are observed at 19.93, 35.25 and 61.77(2 θ) with the distances of 4.45, 2.54 and 1.50 Å, respectively. The RB has a well-defined d₀₀₁ pattern while the d₀₀₁ peaks of AIFe-PILC-B is broad and its intensity lower than RB, which means that AlFe-PILC-B is semi crystalline in nature (since the heterogeneity in the size of the pillars). Also, the presence of a wide signal regarding d_{001} is related to the long range face to face layer aggregation which arisen from the inadequate entrance of ion in the interlayer space [21-23]. An interlayer opening caused by pillaring process were calculated as 8.45 Å for AlFe-PILC-B by subtracting the thickness of SiO₂-Al₂O₃-SiO₂ sheet (9.6 Å) from the d(001) value of pillared clay [7]. The amount of the interlayer expansion for the Fe containing pillared samples slightly larger than the Al pillared samples might be due to the substitution of Al^{3+} by the somewhat larger Fe^{3+} ions in the original Al₁₃-pillars [19].

3.2. FTIR data of samples

The FTIR spectra of the RB and AlFe-PILC-B samples are shown in Fig. 2. The comparative infrared spectra of raw and pillared bentonite are extensively utilized for investigation of the structural changes in clay framework. There are significant differences between the spectra of RB (Fig. 2a) and pillared bentonite (Fig. 2b). The peaks at 3627 and 918 cm⁻¹ are ascribed to the OH stretching of structural hydroxyls and deformation of AlAlOH in the octahedral layers of RB whereas the peaks at 3456 and 1641 cm⁻¹ correspond to the OH stretching and OH deformation of water of RB, respectively. After pillaring, the intensities of these peaks decrease since the removal of the hydroxyl groups and the adsorbed water [8]. The features at 1041 and 1090 cm⁻¹ correspond to the Si-O stretching vibration and the Si-O stretching band (longitudal mode) of tetrahedral sheet. As in the previously reported studies, the original positions and intensities of these peaks were altered by the pillaring of the RB which may be due to the siloxane layers perturbed by pillars. In addition, the vanish of the peaks at 627 and 523 cm⁻¹ belong to coupled Al-O, Si-O (out of plane) and Al-O-Si deformation of bentonite show that the clay layer structure was affected by pillaring process. However, absence of additional peaks suggests that no bond formation occurs between bentonite and pillars [47]. In addition the band at 793cm⁻¹ may reflect the presence and survival of cristobalite after the pillaring process. This state was also supported by PXRD measurements.

3.3 Thermal analysis of samples

The thermal analysis (TG-DTG and DTA) profiles of the samples are shown in Fig. 3. On the curve of RB, two dehydration stages with a total mass loss of 12.26 % in the temperature range of 31-212 °C are noticeable. The removal of adsorbed water with a mass loss of 10.73 % in the first stage 31-142 °C gives rise to an endothermic DTA peak centred at 90 °C and the endothermic feature at 163 °C in the range of 142-212 °C which is accompanied by a mass loss of 1.53 corresponds to the elimination of the water species coordinated to the interlayer cations. Noticeable differences between the thermal curves of RB and AlFe-PILC-B were observed. The total amount of waters removed from pillared bentonite (9.2%) are less than that of RB and the elimination of the adsorbed water from AlFe-PILC-B with a mass loss of 9.2 % in the temperature interval of 31-148 °C, give rise to DTA peaks at 77 °C. Moreover the

removal of cation-coordinated water species is not observed in the pillared clay. It could be concluded that the interlayer cations are completely exchanged with keggion ions and the pillared clay obtained after the calcination has low amount of adsorbed waters. However, dehydroxylation processes of AlFe-PILC-B resulted in a mass loss of 2.6% in the range of 337-731 °C (DTG_{max}=655 °C) The dehydroxylation maxima of pillared bentonite shifts to higher temperature compared to the RB (DTG_{max}=625°C). The position of this peak is very important in estimating thermal stability of the pillar bentonites [7,13]. It is clearly seen that the thermal stability of clay enhanced by the pillars present in the interlayer gallery spacing.

3.4. Textural characterization of samples

The surface areas of clay minerals are related to the numbers and sizes of internal and external pores they contain. The total number of micropores (pore width ≤ 2 nm) and mesopores (pore width, 2-50 nm) has primary importance on the surface areas of clays but the contribution of macropores (pore width≥50 nm) to these characteristics is at negligible level [48]. Nitrogen adsorption-desorption isotherms of samples are illustrated in Fig. 4a and Fig.4b. These isotherms of bentonite samples were similar to those reported by the other authors [30,31,49]. According to the IUPAC classification or or BDDT (Brunauer, Deming, Deming and Teller) classification, the nitrogen adsorption/desorption isotherms of bentonite samples demonstrate Type IV behaviour which is characteristic of mesoporous solids [50]. The most important differences between the nitrogen adsorption isotherms of the RB and AlFe-PILC-B can be seen at relative pressures lower than 0.10. For AlFe-PILC-B, the significant increase in adsorbed volume at low relative pressure (P/P₀<0.01) indicated the presence of micropores [30,31,49]. On the other hand, the isotherms of two samples were similar at relative pressure range of 0.40 to 0.99 and showed H4 type hysteresis loops representing the slit shaped pores and plate-like particles with spaces between the parallel plates, which all closed at a relative pressure of about 0.40 [17]. The mesoporosity in the samples is evident from the presence of hysteresis in the isotherms of adsorption/desorption, which are clearly seen in two samples [51]. The AlFe-PILC-B isotherm is in the narrow shape which depends on the pore size distribution, pore geometry, cristallinity and connectivity of a mesoporous adsorbent. Besides, adsorption jumps in the above isotherms appeared due to the capillary condensation in the mesopore between the relative pressures range of 0.2-0.4 (P/Po) [20,52].

The textural parameters of RB and AlFe-PILC-B samples are shown in Table 1. The specific BET surface area of RB (121.32 m^2/g), which contains the micropore and mesopore surface area of 6.07 m^2/g and 115.25 m^2/g , respectively, increased by ca. 2-fold for AlFe-PILC-B (234.49 m^2/g) which arise from the micropore surface area of 67.96 m^2/g and mesopore surface area of 166.53 m^2/g). This increase was expected because the pillaring process mainly creates microporosity. A more detailed description of the microporous and mesoporous regions of the bentonite samples was obtained from the pore size distributions. Typical micropore and the mesopore size distribution curves (calculated by DFT) of RB and AlFe-PILC-B are presented in Fig. 4c and Fig. 4d, respectively. As shown in the figures, the RB possess a unimodal and a fairly broad pore size distribution around pore width of 68 Å (mesopores), whereas AlFe-PILC-B posses trimodal and more sharp pore size distribution around pore width of 10 Å (micropore), 26 Å (mesopore) and 66 Å (mesopore). This situation shows that the mesoporous structure was slightly influenced but micropore structure was significantly influenced and new additional micropores formed by the pillaring process. The similarity of the mesopore size distributions indicates that the size of the mesopore may depend more on the stacking of the silicate leaves rather than on the interlayer distance [17]. Although, the pillaring process produced a remarkable increase in the micropore volume from 0.001 cc/g to 0.027 cc/g for AlFe-PILC-B, but the total pore volume did not significantly change. In addition, RB has the average pore width of 67.94 Å whereas the value of this parameter decreases to 8.63 Å for AlFe-PILC-B. These results were in great agreement with the nitrogen adsorption/desorption isotherms. The increasement of the surface areas of pillared bentonite may be ascribed to the increasing effect of the formation of the micropores and enlarged cumulative pore volume of micropores.

3.5. Surface acidities of samples

Pyridine has been utilized as a probe molecule for the determination of the chemical nature of acidic sites in the raw and pillared bentonites [15,36,53] The specific IR absorption peaks of adsorbed pyridine in the region of 1700-1350 cm⁻¹ have been used to differentiate between the Brønsted and Lewis sites of RB and AlFe-PILC-B samples (Fig. 5). Following the pyridine adsorption on RB, the peaks at 1635, 1595, 1541, 1492 and 1441 cm⁻¹ were observed. The peaks at 1595 and 1441 cm⁻¹ originated from H-bonded pyridines species whereas the peaks at 1635 and 1541 cm⁻¹ represent the pyridine molecules interacted with the

Brønsted acidic sites. In addition, the prominent peak at 1492 cm⁻¹ mainly originated from the pyridine species held by both the Brønsted and Lewis centres [15,36,53]. The corresponding peak intensities of adsorbed pyridine indicated that Brønsted acidity was predominant in the raw bentonite and these observations are in accordance with the thermal analysis results of pyridine adsorbed onto RB. The unsaturated metal atoms located at the edges of the siloxane layer are the major sources of Lewis acidity for RB while the interlamellar water coordinated to exchangeable cations and the terminal silanols of the clay contribute to the Brønsted acidy. The spectrum of AlFe-PILC-B-Py recorded at 100 °C shows the presence of both Lewis and Brønsted acid sites (Fig. 5b). The most prominent peaks at 1610 and 1451 cm⁻¹ come from the pyridine species coordinated to Lewis acid centres were observed as significantly strengthened whereas the peaks related to the pyridine species protonated at Brønsted acidic centres at 1638 and 1542 cm⁻¹ were observed as slightly increased for AlFe-PILC-B. The formation of AlFe-pillars between the bentonite layers strongly increases the Lewis acidity but do not have further special improvement over the Brønsted acidity. Because the Brønsted acidity come from the clay structure as mentioned above, pillars have a little contribution. IR spectrums of samples clearly show that the surface Lewis acidity of AlFe-PILC-B is greater than that of RB.

Additionally, thermal desorption of pyridine onto bentonite samples was also followed by thermal analyses techniques (TG/DTG) to calculate the acidity of samples and estimate the acidic strength of both Brønsted and Lewis acid centres (Table 2). The desorption of the pyridine species on the bentonite composites in the temperature range of 30-500 °C give rise to three different mass losses depending on the surface acidity of bentonites. The first mass loss in the temperature range of 30-95 °C usually corresponds to the removal of moisture or desorption of physisorbed pyridine on weak acid sites. However, the IR spectra of pyridine adsorbed on bentonite samples did not show any band at 1575cm⁻¹ which is diagnostic of physisorbed pyridine. Thus, this mass loss at near 63°C must be related to desorption of moisture and/or H-bonded pyridine attached to external surface sites. The second and third mass losses in the temperature interval of 100-235°C and 243-357°C are attributed to desorption of pyridine species onto Brønsted and Lewis acid sites, respectively [54,55]. The acidity (A) of the two composites was calculated as mmol pyridine/gram catalyst based on the thermal analysis data. The RB-Py species presents three DTG peaks corresponding to desorption of pyridine at 63, 169 and 280 °C in the temperature ranges of 30-95 °C, 100-235 °C and 243-357 °C with the mass losses of 3.90, 7.81 (together 1.53% mass loss of removal

of water coordinated to the interlayer cation) and 1.33%, respectively. These mass losses are related to the elimination of moisture, removal of protonated pyridine species on Brønsted acid sites and desorption of pyridine from Lewis acid sites (A=0.158), respectively, while the classic DTG peak at 621 °C corresponds to dehydroxylation process. RB has more Brønsted acid sites (A=0.77) than Lewis acid sites (A=0.158). For AlFe-PILC-B, in the temperature interval of 100-235 °C, the removal of pyridine species from Brønsted acid sites (A= 0.827) with a mass loss of 6.54% gives rise to a DTG peak at 174 °C. In addition, the DTG peak at 352 °C with a mass loss of 6.80% corresponds to desorption of pyridine from Lewis acid sites (A=0,872). It is clearly seen that the Lewis acidity of the RB (A=0.158) is enhanced by ca 6-fold for AlFe-PILC (A=0,872) whereas the Brønsted acidity of RB is slightly increased by pillaring process. The increase of Lewis acidity is due to the formation of pillar oxides in the interlayer region as interpreted in FTIR results. Furthermore, the pyridine species coordinated to the Lewis centres gets extra thermal stability of about 72°C for AlFe-PILC-B compared to RB. In addition, the total acidity value of RB (0.928) remarkably increased to 1.699 for AlFe-PILC-B with the pillaring process.

3.6. Friedel–Crafts acylation

Friedel–Crafts type acylation of aromatic compounds to aromatic ketones is one of the most important synthesis methods used in organic chemistry [37-42]. As an example, this reaction is widely used to test the acidic properties of catalyst [42]. To test the catalytic activity of our samples, we studied the Fridel-Crafts benzoylation of benzene with benzoyl chloride in the presence of raw and pillared bentonites (Fig. 6). Benzene and benzoyl chloride were separately treated with raw and AlFe-PILC-B bentonites as the catalysts at 80 °C for 24 h. No benzophenone formation was observed by ¹H-NMR spectroscopy when raw bentonite was used as catalyst, whereas benzophenone was obtained with the yield of 46% in the case of AlFe-PILC-B utilization. Benzophenone was purified by means of column chromatography and characterized by its ¹H and ¹³C NMR spectra, shown to be identical with an authentic sample. The amount of benzophenone yield significantly depends on the concentration and strength of the Lewis acidic sides of bentonite samples.

4. Conclusion

The XRPD pattern showed that the pillaring of bentonite caused an expansion of basal spacing from 15.80 to 18.05 Å. The original positions and intensities of peaks at 1041 and 1090 cm⁻¹ correspond to the Si-O stretching vibration and the Si-O stretching band of tetrahedral sheet were altered by the pillaring of the RB. The pillars in the interlayer gallery spacing enhanced the thermal stability of raw bentonite. Nitrogen adsorption-desorption isotherms of samples showed that the mesoporous structure was not significantly influenced but a new micropores were formed by pillaring process. The formation of FeAl-pillars into the bentonite layers on AlFe-PILC strongly increased especially the Lewis acidity but do not have further special advantage over the Brønsted acidity. The present data shows that the AlFe-pillared bentonite material can be used as a solid catalyst for Friedel Crafts acylation of aromatic hydrocarbons. Also, the data obtained in this study may provide further insight into heterogenous catalysis studies and may be utilized for developing new eco-friendly solid catalysts.

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Figure Legends:

CCK

Fig. 1. PXRD patterns of the bentonite samples (a) RB, (b) AlFe-PILC-B

Fig. 2. FTIR spectra of the bentonite samples (a) RB, (b) AIFe-PILC-B

Fig. 3. DTA, DTG and TG curves of bentonite samples (a) RB, (b) AIFe-PILC-B

Fig. 4. Nitrogen adsorption-desorption isotherms of samples (a) RB, (b) AlFe-PILC-B and typical micropore and the mesopore size distribution curves of samples (c) RB, (d) AlFe-PILC-B

Fig. 5. FTIR spectra of the pyridine adsorbed bentonite samples (a) RB-Py, (b) AIFe-PILC-B-Py

Fig. 6. Benzoylation of benzene with benzoyl chloride over the AlFe-PILC-B catalyst

Table Captions

Table 1. Textural parameters of bentonite samples

Table 2. Thermal analysis data of the pyridine adsorbed bentonite samples

Table 1. Textural parameters of bentonite samples

C

	SBET	t ^{βµρ}	BJHSmp	$_{t}V^{\mu p}$	_{вјн} V ^{mp} (cm³g⁻
Sample	(m ² g ⁻¹)	(m ² g ⁻¹)	(m ² g ⁻¹)	(cm ³ g ⁻¹)	1)
RB	121.32	6.07	115.25	0.002	0.249
AlFe-PILC-B	234.49	67.96	166.53	0.027	0.244

SCI

Sample	Temp. range	Mass loss (%)	DTG _{max.}	Acidity (A)	Thermal process
	(°C)			(mmol/g _{cat})	0
RB-Py	30-95	3.90	63		-Removal of moisture and H-bonded pyridine
	100-235	7 01	160	0 770	-Desorption of Py from Brønsted sites and
		7.81	169	0.770	removal of coordinated water (1.53%)
	243-357	1 22	200	0.159	-Desorption of Py from Lewis sites
	260 601	1.55	280	0.158	-Dehydroxylation
	300-091	5.30	621		
	22.01	0.02	(0)		Demovel of maisture and U handed muriding
Alfe-PILC-B-Py	32-91	0.92	60		-Removal of moisture and H-donded pyridine
	10-235	6.54	174	0.827	-Desorption of Py from Brønsted sites
	240-400 6.80 352	0.072	-Desorption of Py from Lewis sites		
	468-705	1.82	650	0.872	-Dehydroxylation
	C				

Table 2. Thermal analysis data of the pyridine adsorbed bentonite samples













Highlights

- The AlFe-pillared bentonite catalyst was characterized by various techniques.
- The new micropores and Lewis acidic sites were formed by pillaring process.
- The AlFe-pillared bentonite as catalyst was used in the benzoylation of benzene with benzoyl chloride.
- The AlFe-pillared bentonite is a promising eco-friendly catalyst in organic reactions