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Research Paper

Surface Activation of Calcium Bentonite by Acid Treatment

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**Abstract:** Calcium bentonite was treated with sulphuric acid of 3M concentration by mechanical stirring and thermal refluxing condition followed by calcination at 500°C for 1h. The physico-chemical characteristics of acid leached calcium bentonite were studied by different instrumental analytical techniques. The effect of thermo-acidic treatment is more pronounced as compared to mechano-acidic treatment. XRF and FTIR studies indicate that acid treatment leads to the removal of the octahedral Al<sup>3+</sup> and other cations. XRD of acid treated calcium bentonite infer that acid treatment with mechanical stirring and heating provoked an amorphization of crystalline clay. The acid treatment increased the Si/Al ratio, surface area and water content. Solids thus obtained by acid treatments can be used as promising adsorbents and catalyst supports for acid catalysed reactions.

**Keywords:** Surface Activation, Calcium bentonite, acid treatment, adsorbent, catalyst

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Introduction

Solid acids are one of the important categories of heterogeneous catalysts used in many industrial chemical processes starting from the largest chemical process of catalytic cracking in petroleum refining to the synthesis of various fine chemicals owing to their high productivity, easy separation, reusability and eco-friendly features. Solid acid catalyst carries two types of acid sites such as Bronsted acidity and Lewis acidity. Bronsted acid sites of the solid acid can donate, or at least partially transfer a proton which becomes attached with surface anions and the Lewis acid sites of the solid acid catalyst must be able to accept an electron pair. Some examples of solid acid catalysts are alumina, silicalite-I, chlorinated alumina, H-zeolites, heteropoly acid, niobic acid, solid phosphoric acid, sulfated zirconia, clay etc.<sup>1,2</sup>. Among the different solid acid catalysts, clay materials are an important class of natural occurring solid acid catalysts, which can function as both Bronsted and Lewis acids in their natural and ion-exchanged form and find diversified application in different environmentally benign green chemistry<sup>3</sup>.

Clay is a fine grained natural rock or soil material that combines one or more clay minerals with traces of

metal oxide and organic matter found abundantly on earth's crust. Chemically it consists essentially of hydrated silicates of aluminum. They have a layered structure, where different layers of silica tetrahedra and hydrated alumina octahedra are bound together by some covalent and van-der Waal's forces. Among the different clay materials, bentonite is a phyllosilicate clay consisting mostly of Montmorillonite. Bentonite usually forms from weathering of volcanic ash, mostly in the presence of water. For industrial purposes, two main classes of bentonite exist: Na and Ca bentonite. Among these two, calcium bentonite is one of the clay materials widely used for a large number of applications. Calcium bentonite is the major mineral component of Semectite, which may usually contain quartz and mica and also, less frequently feldspar, illite, Montmorillonite, limonite, calcite, gypsum, haematite, graphite<sup>4</sup>.

Chemically calcium bentonite is a 2:1 layer sheet structured with one octahedrally coordinated gibbsite [Al<sub>2</sub>(OH)<sub>6</sub>] sandwiched between two sheets of tetrahedrally coordinated silicate [SiO<sub>4</sub>]<sup>4-</sup> sheet. Its theoretical formula is Al<sub>2</sub>O<sub>3</sub>.4(SiO<sub>2</sub>).H<sub>2</sub>O (other formula is [Si<sub>4</sub>Al<sub>2</sub>O<sub>10</sub>(OH)<sub>2</sub>].H<sub>2</sub>O), which has a molecular weight of 360.31 gm/mol<sup>4</sup>.

Calcium bentonite is a useful adsorbent of ions in solution, as well as fats and oils. It is the main active ingredient of fuller's earth, probably one of the earliest industrial cleaning agents.

Bentonites have very ample and attractive properties which gives them a wide and diverse range of uses. Most importantly, Calcium bentonite has wide range of applications in the field of organic synthesis as a solid acid catalyst. The catalytic properties of Bentonites are a direct result of their high specific surface area and localization of acid center. It can catalyze many organic reactions including synthesis of Aziridines, benzimidazoles, and different aryl and alkyl esters to enhance the quality of product<sup>4</sup>. In addition, recently there is widespread interest in the use of surface modified clays against the dominant use of microporous zeolite acid catalysts in modern petrochemical processes, due to low cost and suitability of pore structure and dimension for cracking of larger molecule even. Different methods have been suggested in literature to improve the properties of clay materials which include among others mechano-chemical activation<sup>5-7</sup>, intercalation<sup>8,9</sup>, thermo-chemical treatment<sup>10,11</sup> and chemical activation<sup>12-14</sup>.

Acid activation which involves treatment of the clays with inorganic acids, thus altering the chemical composition and the structure of the clays has been widely studied as a chemical treatment method for the improvement of the surface and catalytic properties of clays. The acid treatment is beneficial in terms of increased surface area, porosity and number of acid centers with respect to the parent clays. The acid treated clays are composed of a mixture of non-attacked clay layers and a hydrous, amorphous, and partially protonated silica phase that are inexpensive in different industrial uses as sorbents or as catalyst supports<sup>13</sup>.

Literature reveals works on the systematic examination of different clay materials prepared from mechanically and thermally amorphized clay by acid leaching. However, a systematic analysis of the mechano-chemical and thermo-chemical activation of Ca-bentonite with sulfuric acid is sparsely found in the literature. So, the objective of this work is to study the behavior of calcium bentonite clay treated with sulfuric acid under mechanical stirring and refluxing condition separately. The changes in physico-chemical properties are studied by different instrumental techniques such as XRF, XRD, FTIR, TGA, SEM and BET surface area analyzer<sup>13,14</sup>.

### Material and Methods

The calcium bentonite clay used in this experiment was procured from Benzenikx Pharma & Industrial Products Pvt. Ltd., Hyderabad, India. The sample was

used as such without any further modification for the surface modification. The chemical composition of the sample is as follows: SiO<sub>2</sub> 53.02%, Al<sub>2</sub>O<sub>3</sub> 20.34%, Fe<sub>2</sub>O<sub>3</sub> 9.39%, MnO 0.08%, CaO 4.85%, ZnO nil, Na<sub>2</sub>O 0.33%, TiO<sub>2</sub> 1.14%, P<sub>2</sub>O<sub>5</sub> 0.03%, V<sub>2</sub>O<sub>5</sub> 0.09% and loss on ignition 10.72%. The sulfuric acid used in this experiment was procured from Merck specialties Pvt. Ltd., Worli, Mumbai, India and product name is EMPLURA Sulfuric acid. The composition of product is as follows: Assay (H<sub>2</sub>SO<sub>4</sub>) 95-98%, residue on ignition as sulfate ≤ 0.005%, heavy metal as Pb ≤ 0.001%.

### Surface activation

The acid activation of calcium bentonite clay was carried out by two ways i.e. by mechano-chemical treatment and thermo-chemical treatment. In first case, the chemical activation was carried out by adding 30 g of the clay sample to 300 ml of 3N sulfuric acid solution and stirring without heating under the atmospheric pressure in a round bottom flask using a hot plate cum magnetic stirrer for 4h. In the second experiment, the chemical activation was carried out by adding 30 g of the clay to 300 ml of 3N sulfuric acid solution and refluxing at about 80°C under the atmospheric pressure in a round bottomed flask equipped with a reflux condenser for 4 h. The clay suspension obtained in both case was then rapidly quenched by adding 500 mL ice cold water. The contents of both flasks were then filtered, repeatedly washed with distilled water to remove any unspent acid, dried in an oven, calcined at 500 °C for 1 h and ground in a mortar pastel to powder form. The untreated calcium bentonite sample is referred to as CB and treated samples are referred to as mechano-acid treated calcium bentonite (MACB) and thermo-acid treated calcium bentonite (TACB).

### Characterization techniques

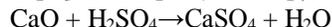
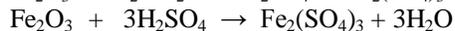
The original and surface modified calcium bentonite clay materials were characterized by different instrumental techniques as follows. The X-ray fluorescence spectroscopy (XRF) was carried out using a Model-PW2400 of Phillips make, with X-ray tube of rhodium anode and scintillation detector with a current 40 mA and voltage 40 kV. X-ray diffraction (XRD) of the samples were taken using Philips analytical X-ray instrument, X'PertMPD (PW 3020 vertical goniometer and PW 3710 MPD control unit) employing Bragg-Brentano para focusing optics in the range of 10–70° and scanning rate 2°/min.. Fourier transformed infrared spectroscopy (FTIR) were recorded on a Perkin-Elmer infrared spectrophotometer as KBr pellets with resolution of 4 cm<sup>-1</sup>, in the range of 400–4000 cm<sup>-1</sup>. Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) were carried out with a SHIMADZU DTG-60/60H instrument at a constant heating rate of 10°C/min operating in a stream

of N<sub>2</sub> atmosphere with a flow rate of 40 mL/min from 35°C to 600°C. Scanning electron microscope (SEM) of the sample were taken using JEOL-JSM 5600LV microscope, equipped with a 6587 EDS (energy dispersive X-ray spectrometry) detector, using an accelerating voltage of 15 kV and sorptometric studies were done with an autosorb BET apparatus from Quantachrome Corporation. Nitrogen adsorption-desorption measurements (BET method) were performed at liquid nitrogen temperature (-196°C). Before each measurement, the samples were out gassed first at 200°C for 2 h, at  $5 \times 10^{-3}$  Torr and then at room temperature for 2h, at  $0.75 \times 10^{-6}$  Torr. The isotherms were used to determine the specific surface areas using the BET equation.

## Results and discussion

### XRF Result

The XRF analysis was carried out to know the chemical compositions of the clay and the subsequent chemical changes that occurred due to treatment. Table 1 shows the results of chemical analysis of the parent and treated calcium bentonite. The parent clay contains alumina and silica which are in major quantities where as other oxides such as manganese oxide, calcium oxide, potassium oxide, zinc oxide and titanium oxide are present in trace amounts. After the acid treatment, it was observed that the composition of the calcium bentonite changes considerably. The Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CaO contents decreased and SiO<sub>2</sub> content increased in the acid treated calcium bentonite. According to literature, the reaction between calcium bentonite and sulphuric acid is described by the chemical equation. From the reaction it conclude that during leaching process, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and CaO react with sulphuric acid solution produces sulphates which are soluble in water and due to this fact, the amount of alumina and iron (III)oxide contents decrease during thermo-chemical process. Similarly, CaO, which under goes acidification, soluble as CaSO<sub>4</sub> in water and completely wash out during thermo-chemical process. But silica content increases due to makeup the deficiency of alumina and some trace elements.



It can be observed that the concentration of ZnO, MnO, V<sub>2</sub>O<sub>5</sub>, P<sub>2</sub>O<sub>5</sub> remained almost unchanged with acid reagent. The extent of leaching depends on the type of treatment (mechano-chemical/thermo-chemical). For example, with 3N H<sub>2</sub>SO<sub>4</sub> treatment with mechanical stirring and heating, the Al<sub>2</sub>O<sub>3</sub> content decreased from 20.34 to 17.40% and 15.34% respectively, whereas the SiO<sub>2</sub> content increased from 53.02 to 57.52% and 65.04% respectively. Thus the Si/Al ratio of the calcium bentonite treated with acid increases in the same trend. The leaching process is more extensive as

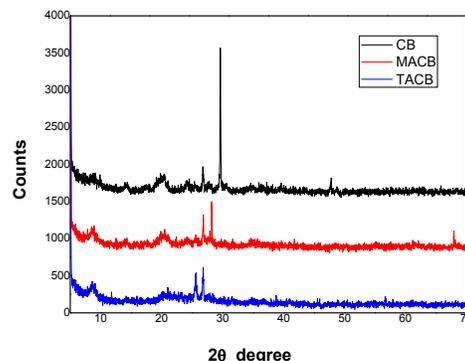
compared to mechanical stirring. The XRF study clearly indicated that leaching occurred in a sequential manner due to attack at tetrahedral layer resulting in the dealumination of clay due to reaction with acid along with mechanical stirring and supply thermal energy<sup>13-15</sup>.

**Table 1: XRF analysis of calcium bentonite**

Components (%)	CB	MACB	TACB
Al <sub>2</sub> O <sub>3</sub>	20.34	17.40	15.34
Fe <sub>2</sub> O <sub>3</sub>	9.39	7.71	4.65
TiO <sub>2</sub>	1.14	1.27	1.26
SiO <sub>2</sub>	53.02	57.52	65.04
Na <sub>2</sub> O	0.33	0.35	0.36
CaO	4.85	3.65	0.00
P <sub>2</sub> O <sub>5</sub>	0.03	0.03	0.03
V <sub>2</sub> O <sub>5</sub>	0.09	0.09	0.09
ZnO	0.00	0.00	0.00
MnO	0.08	0.08	0.08
LOI	10.72	11.90	13.15

### XRD Result

The structural changes that occurred in the clay material due to acid treatment were studied using X-ray diffraction technique. Figure 1 shows the XRD profiles of the CB, MACB, TACB. The parent clay shows well defined reflections at 2θ value of 30°, which correspond to the reflections from [0 0 1], which is typical characteristic peak of calcium bentonite. Again the peaks corresponding to the 2θ value 8-10°, 12-15°, 20-24°, and 25-32° may vary for calcium bentonite from different origin. Upon acid treatment the peak intensity of the clay was found to decrease progressively. This is due to the structural disorder that occurred owing to the acid treatment, which affects the crystalline character of the clay. Again upon thermo-chemical treatment the peak intensity of the clay was found to be further decreased as compared to mechano acid treatment and disorderliness of structure occurred i.e., crystalline structure changed to amorphous form.



**Figure 1: XRD analysis of different calcium bentonites**

The narrowing of the peak may be related to the increase of crystallite size and/or the decrease of the mean lattice strain. It was observed that the calcium bentonite clay treated with 3N sulphuric acid with mechanical stirring does not show any well-defined peak at  $2\theta$  value of  $30^\circ$  but a narrow peak shifted to  $2\theta$  value  $28^\circ$  in the X-ray diffractograms. Similar observation was found in case of thermo-acid treatment where it show narrow peak at  $2\theta$  value of  $26^\circ$ . The shifting of peaks occur in both the case with respect to CBensures the structural changes from crystalline to amorphous. Since leaching is quite severe in thermo-acidic treatment, more shifting of peak was observed in this case<sup>13</sup>.

**FTIR Result**

The FTIR spectrums of different calcium bentonite samples are shown in Figure 2 (a,b,c) and the corresponding band assignments are shown in Table 2. In the O-H stretching region, the parent and acid treated clay shows three prominent bands at 3429, 3435, 3437 and 3580  $\text{cm}^{-1}$  corresponds to Al-OH stretching. Inner hydroxyl groups, lying between the tetrahedral and octahedral sheets give the absorption at 3429  $\text{cm}^{-1}$ . A strong band at 3435  $\text{cm}^{-1}$  and 3437  $\text{cm}^{-1}$  is related to the in phase symmetric stretching and . The band observed at 3429  $\text{cm}^{-1}$ , assigned to the high amount of water physisorbed on the surface of the clay. There was not much variation in the peak pattern for acid treated and thermo-chemical treated calcium bentonite.

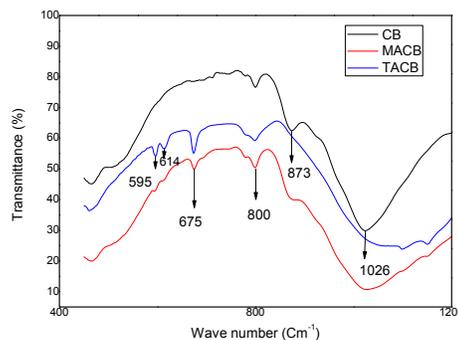
For the 3N  $\text{H}_2\text{SO}_4$  treated CB the structural hydroxyl vibration band is extremely weak. In the bending region mode, the clay materials show a series of IR bands with peak maxima at 1638, 1630, 800, 675 and 614  $\text{cm}^{-1}$ . The peak at 1630  $\text{cm}^{-1}$  is quite intense is attributed to the bending vibration ( $\text{H-O-H}_{\text{bend}}$ ) mode of physisorbed water on the surface of free silica produced due to leaching. This peak was found to be absent in case of the acid treated clay due to structural disintegration. The IR peaks at 595, 1026 and 3435  $\text{cm}^{-1}$  can be assigned to the Si-O-Al, Si-O<sub>str</sub> and Al-O-H vibration of the clay sheet. The high intense 800  $\text{cm}^{-1}$  peak due to vibrations of inner OH groups was found to be drastically reduced for 3N  $\text{H}_2\text{SO}_4$  treated clay.

**Table 2: Important IR bands of calcium bentonite clay with their possible assignments**

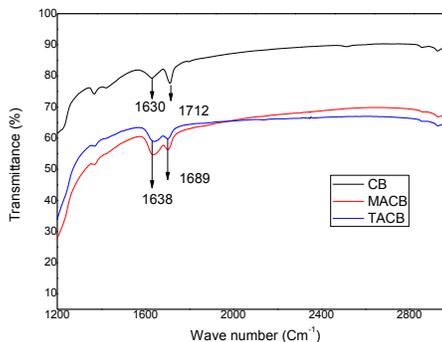
Band ( $\text{cm}^{-1}$ )	Assignments
3429	Al-O-H <sub>str</sub> (physisorbed water)
3435, 3437, 3580	Al-O-H <sub>str</sub> (structural hydroxyl groups, octahedral)
1630	H-O-H <sub>bending</sub> (physisorbed)
873	Al-Al-OH <sub>str</sub>
1026, 800	Si-O <sub>str</sub>
755	Si-O-Al <sub>str</sub>

614, 595	Si-O <sub>str</sub> , Si-O-Al <sub>str</sub>
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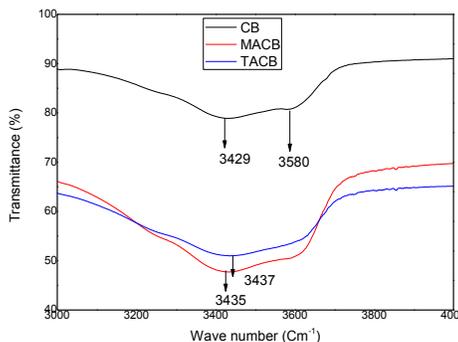
It can be concluded that, the thermo-chemical treatment i.e, dealumination process is facilitated rapidly, during acid treatment, because of this fact alumina content decreased. Again well resolved strong bands in the 1050-1000  $\text{cm}^{-1}$  region is due to Si-O stretching in untreated calcium bentonite which changed in shape and position due to structural changes in the tetrahedral cations. The FTIR result is in clear agreement with the XRF studies which indicates sequential degradation of the clay sheet upon acid treatment along with mechanical stirring and thermal heating<sup>13,14,16</sup>.



**Figure 2 (a): FTIR of different CB**



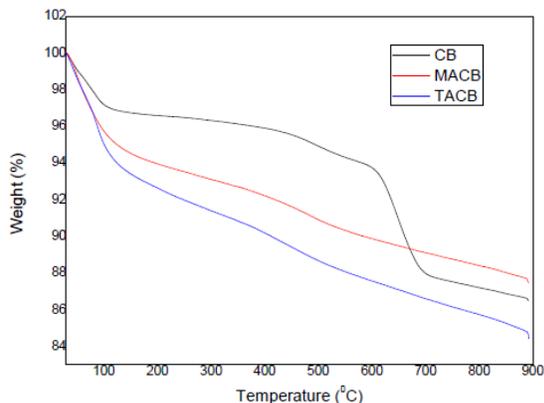
**Figure 2 (b): FTIR of different CB**



**Figure 2(c): FTIR of different CB**

**TGA result**

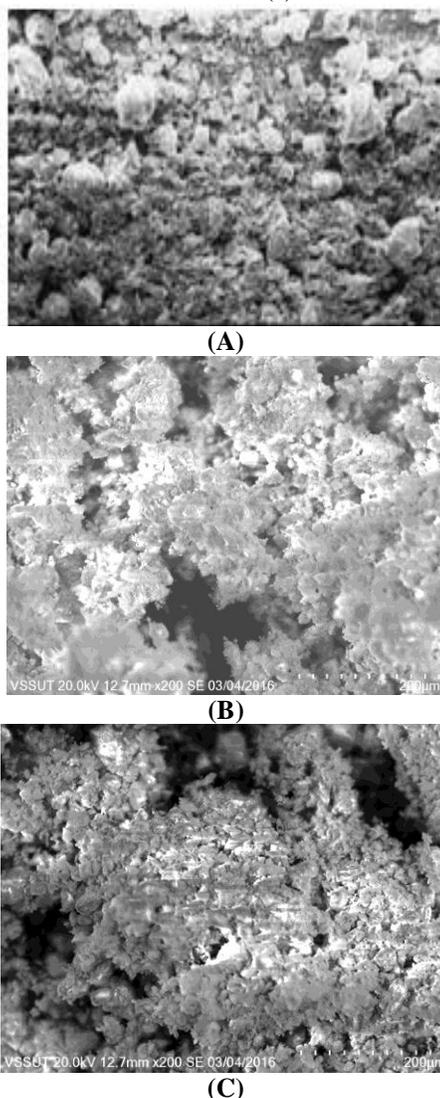
The TGA curves (Figure 3) of the pure, mechano-acid treated and thermo-acid treated calcium bentonite show two well-defined weight loss regions due to the loss of physisorbed water (below 200°C) and dehydroxylation of coordinated and structural water (above 450°C). In general, clay materials contain three kinds of water molecules in their structure. The physisorbed and interlayer water are loosely bound and are mobile that they can be removed by heat treatment below 200°C. The water molecule present in the first coordination sphere of the interlayer ions is strongly bonded and they require higher temperature in the range of 300–500°C for their removal. Finally the structural hydroxyl groups can condense and dehydrate in the temperature range of 500–800°C. In the present study, the low temperature water loss can be assigned to the physisorbed water, whereas the high temperature weight loss is due to the dehydration and dehydroxylation of the clay sheet. Comparing the TGA profile of the parent and the mechano-acid treated clay; it was observed that acid treatment increased the amount of physisorbed water. This may be due to the fact that acid treatment increased the amount of amorphous silica and also surface area which made the water adsorption higher. In the high temperature weight loss regions however, the percentage loss is lower for acid treated clay as compared to the parent clay. This is due to the removal of the octahedral Al ions along with the concurrent removal of structural hydroxyl groups due to acid treatment. Following TGA analysis shows that about 96.94% weight was obtained at 115.5°C in the case of untreated calcium bentonite whereas about 95.5% weight was obtained at 106.23°C in the case of mechano-acid treated calcium bentonite. But in case of thermo-acid treated calcium bentonite, about 94.72% weight was obtained at 105.62°C. From the above data it is concluded that rate of weight loss is more in case of mechano-acid treated and further increased in thermo-acid treated calcium bentonite as compared to untreated calcium bentonite<sup>13, 14</sup>.



**Figure 3: TGA analysis of calcium bentonite**

**SEM Result**

The scanning electron micrographs of the different calcium bentonite clay samples are presented in Figure 4[(a),(b),(c)] which shows the morphological features. The SEM micrograph of CB reveals the presence of large particles that appeared to have been formed by several flaky particles stacked together in form of agglomerates. The SEM images of CB, acid treated CB, thermal and acid treated CB show different particle morphology. The micrograph of CB(a) indicates that the particles are arranged in a disaggregated or distinct manner whereas the micrograph of acid treated CB(b) shows that the particles are well-bonded and become agglomerate. Then the SEM micrograph of thermal and acid treated CB(c) indicates that, by thermo-chemical treatment the agglomeration of particles becomes increased rather than detached particles and well-bonded than (c)<sup>15</sup>.



**Figure 4: (a) SEM of CB (b) SEM of MACB (c) SEM of TACB**

### BET Surface area Result

According to BET theory, physical adsorption of gas molecules on a solid surface in a given pressure allows to determine the surface area. BET surface area increased with increasing acid strength, which is summarised in Table 3. Upon 3N sulphuric acid treatment by mechanical stirring, the surface area of the original clay increased from 146 to 193 m<sup>2</sup>/g and with thermo- acid treatment the surface area increased to 290 m<sup>2</sup>/g which is about two times greater than the untreated calcium bentonite. As the surface area increased with acid treatment either by mechano-chemically or by thermo-chemically, the reactivity of catalysts increase as well as catalytic/chemical reaction becomes faster than original.

**Table 3: BET surface area analysis of calcium bentonite**

Catalyst	Surface area m <sup>2</sup> /g
CB	146
MACB	193
TACB	290

### Conclusion

In this work, we have studied the effect of the sulphuric acid with mechanical stirring and thermal refluxing condition on the structural and chemical properties of calcium bentonite clay. The changes observed in this treatment were more prominent in thermo-acidic condition than mechano-acidic condition.

- The XRF and SEM studies indicated clearly the leaching and disintegration of the clay sheet upon thermo-chemical treatment. XRD studies of the acid treated clay indicated the structural transformation of the clay sheet upon acid treatment. The pure clay is crystalline, whereas the crystallinity and the interlayer structure of the clay material were found to be altered with acid treatment and became amorphous.
- On acid treatment, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and Na<sub>2</sub>O contents in the acid treated material decreased progressively simultaneously increasing the SiO<sub>2</sub> content.
- FTIR study of the acid treated clay shows the presence of several kinds of structural OH groups whose peak position and intensity changes with increase in acid concentration. Acid treatment did not cause much variation in the peak pattern. However thermo-acid treatment in same acid strength the peak intensity was found to decrease progressively and indicating the dehydroxylation and successive leaching of the Al ions from the octahedral layer. Since the OH groups play a predominant role in clay catalysis, the acid treatment may be beneficial in terms of generation of new acidic sites.
- Again, the BET surface area analysis of the samples indicated the increase in surface area with acid

treatment and further increased with thermo-acidic treatment.

Thus, this method can be useful for manufacturing a surface active and high surface area material which can be used for catalyst as well as an adsorbent.

### References

1. Guido B., Acid catalysts in industrial hydrocarbon chemistry, *Chem. Rev.*, **107(11)**: 5366 (2007)
2. Corma A., Inorganic solid acids and their use in acid-catalyzed hydrocarbon reactions, *Chem Rev.*, **95(3)**: 559 (1995)
3. Gopalpur N., Organic synthesis using clay and clay-supported catalysts, *Applied Clay Science*, **53**: 106–138 (2011)
4. www.market izer.com. Uses and application of bentonite. Quiminet. (2012)
5. Dragsdorf R.D., Kissinger H.E. and Perkins A.T., An X-ray study of the decomposition of kaolinite, *Soil Science*, **71**: 439 (1951)
6. Gregg S.J., Parker T.W. and Stephens M.J., The grinding of kaolinite: II. *J. Appl. Chem. (London)*, **4**: 666 (1954)
7. Temujin J., Burmaa G., Amgalan J., Okada K., Jadambaa Ts. and MacKenzie K.J.D., Preparation of porous silica from mechanically activated kaolinite, *J. Porous Mater.*, **8**: 233 (2001)
8. Ledoux R.L. and White J.L., Infrared studies of hydrogen bonding interactions between kaoline surface and intercalated potassium acetate, hydrazine, formamide and urea, *J. Colloid Interface Science*, **21**: 127 (1966)
9. Horvath E., Kristof J., Frost R.L., Jakab E., Mako E. and Vagvolgyi V., Identification of super active centers in thermally treated formamide–intercalated kaolinite, *J. Colloid Interface Science*, **289**: 132 (2005)
10. Lussier R.J., A novel clay-based catalytic material—preparation and properties, *J. Catalyst*, **129**: 225–237 (1991)
11. Chaisena A. and Rangsriwatananon K., Effect of thermal and acid treatment on some physico-chemical properties of lamping diatomite, *J. Science Technology*, **11**: 289 (2004)
12. Rhodes C.N., Franks M., Parkes G.M.B. and Brown D.R., The effect of acid treatment on the

- activity of clay supports for  $\text{ZnCl}_2$  alkylation catalysts, *J. Chem. Soc. Chem. Communication*, **12**: 804 (1991)
13. Panda A.K., Mishra B.G., Mishra D.K. and Singh R.K., Effect of sulphuric acid treatment on the physico-chemical characteristics of kaolin clay, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **363**, 98 (2010)
  14. Kumar S., Panda A.K. and Singh R.K., Preparation and characterization of acids and alkali treated kaolin clay, *Bulletin of Chemical Reaction Engineering & Catalysis*, **8**:61 (2013)
  15. Nascimento A.R., Alves J.A.B.L.R., Melo M.A.F., Melob D.M.A., Souzad M.J.B. and Pedrosae A.M.G., Effect of the Acid Treatment of Montmorillonite Clay in the Oleic Acid Esterification Reaction, *Materials Research*, **18**: 283 (2015)
  16. Miller F.A., Wilkins C. H., Infrared Spectra and Characteristic Frequencies of Inorganic Ions. *Analytical Chemistry*, **24**: 1253 (1952).