

Texture and Microstructure of Chitosan-Treated Bentonite and its Calcined products

Mohd Zobir bin Hussein¹, Mohd Ambar Yarmo², Muhammad Zaki Hj Abd Rahman¹,
Zulkarnain Zainal¹ and Adrian Ang Sang Liang¹

¹Jabatan Kimia, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

²Jabatan Kimia, Universiti Kebangsaan Malaysia, 43000 Bangi, Selangor, Malaysia

(Received 6 September 2000)

Abstrak. Bentonit terawat kitosan (CTB) telah disediakan dengan penuaan bentonit dalam larutan 2 % kitosan dalam asid asetik. Corak pembelauan sinar-X bagi CTB menunjukkan puncak pembalikan yang tajam dengan keamatan tinggi jika dibandingkan dengan bahan pemulanya, bentonit. Analisis CHNS menunjukkan CTB hanya mengandungi 2.6 % karbon. Ini menunjukkan bahawa interkalasi kitosan ke dalam lapisan silikat secara terus tidak begitu mudah berlaku dan berkemungkinan kitosan hanya terjerap dipermukaan bentonit sahaja. Kajian spektroskopi fotoelektron sinar-x (XPS) menunjukkan bahawa inilah yang sebenarnya terjadi, tidak terdapat kandungan nitrogen dalam sampel CTB yang telah dipunarkan. Ini menunjukkan bahawa kitosan telah tidak terinterkalasi ke dalam lapisan silikat, dan pertambahan keamatan XRD hanyalah akibat daripada pembentukan hablur yang lebih baik bagi CTB yang terhasil akibat rawatan tersebut. Namun begitu tekstur dan luas permukaan bagi CTB berubah, di mana luas permukaan BET dan liang mikronya menurun jika dibandingkan dengan bahan pemulanya, daripada 35 m²/g kepada 13 m²/g bagi BET dan daripada 13 m²/g kepada 2 m²/g bagi luas permukaan liang mikronya. Pengkalsinan CTB telah dilakukan pada suhu (100-1000) °C dan hasilnya menunjukkan bahawa luas permukaan liang mikro dan BETnya bertambah dengan pertambahan suhu pengkalsinan sehingga mencapai satu takat optimum pada 500 °C (45 m²/g dengan kandungan 15 % luas permukaan liang mikro). Seterusnya, luas permukaan bahan tersebut menurun dengan suhu. Morfologi permukaan bagi CTB menunjukkan struktur gumpalan tidak berliang dan padat, dan struktur ini hanya berubah menjadi struktur yang lebih berliang hanya apabila sampel tersebut dipanaskan pada suhu yang tinggi, disekitar 1000 °C.

Abstract. Chitosan-treated bentonite (CTB) was prepared by aging bentonite in a 2 % chitosan in acetic acid solution. The resulting XRD pattern of CTB shows a sharper and higher intensity compared to the XRD pattern of the precursor, bentonite. CHNS analysis showed that CTB contains only 2.6 % carbon. This indicates that intercalation of chitosan into the bentonite, a layered silicate did not take place easily. Probably chitosan was only adsorbed on the surface of the bentonite. XPS analysis indicated that this was the case, and no nitrogen could be detected in the etched CTB sample. Chitosan was not intercalated into the silicate interlayer, and the increase of the XRD intensity was only due to a better crystallinity of CTB as a result of the treatment. In addition, the texture and surface area of the CTB changed in which the BET and micropore surface area decreased compared to the precursor, from 35 m²/g to 13 m²/g for BET, and from 13 m²/g to 2 m²/g for micropore surface area. Calcination of CTB was performed at temperatures of 100-1000 °C and resulted in an increased of BET and micropore surface area with calcination temperature, with an optimum at 500 °C (45 m²/g with 15% micropore surface area). Thereafter, the surface area decreased with temperature. Surface morphology of CTB showed a non-porous agglomerate structure and this structure was changed to a porous one only when the sample was heated to 1000 °C.

Key words : bentonite, clay, chitosan, surface area, porosity, SEM.

Introduction

Chitosan, a polycationic polymer and waste product from the seafood processing industry, is an abundant natural resource that has, as yet, not been fully utilized. Advantages of this natural biopolymer include availability, low cost, high biocompatibility, biodegradability and ease of chemical modification. Chitosan can be used for example in water treatment, pharmaceutical products, agriculture and membrane formation [1], to name a few. Apart from chitosan, clay is another abundant raw materials which can be

exploited to be used in various industries for separation and adsorption processes. One of the members of these types of clay is bentonite.

The term "bentonite" was first used by Knight in 1889 following a discovery of highly colloidal plastic clay near Fort Benton in the cretaceous bed of Wyoming [2]. Bentonite is a naturally occurring cationic clay, which can be processed or modified to tailor its properties so that it is suitable for various applications and uses. As it is or with some added chemicals or modifications, bentonite can be used as

rotary mud, filling and oil deodorising, civil construction, foundry, palletizing, bleaching, anticaking medium for certain granular fertilizer, binding medium in agglomeration of cattle feed, pesticides, mineral oil and alkylation of phenols.

Modifications of bentonite by intercalation or sorption has been the subject of interest by many researchers, as the property of resulting materials, may enable them to be used in various application in science and technology.

Work was done to form nanocomposite materials by intercalation of organic or polymer guests into the layered silicate host of bentonite. For example, a novel polyaniline-bentonite layered nanocomposite has been prepared and has potential applications as electrode material for electrochemical battery [3]. Similarly, modifications were also done using various guests such as epoxy polymer [4] and polyacrylate [5].

Apart from intercalation with organic species or polymers, sorption and/or pillaring with inorganic species or polycations are other popular routes of bentonite modification. Cross-linked montmorillonite was prepared by reacting homoionic sodium form of bentonite with high molecular weight polyhydroxy-aluminum complex. The complex was prepared by controlled hydrolysis of alumina macrocation. The intercalated clay was thermally treated to convert the hydroxy cations to oxide pillars of 19 Å height and stable up to 500 °C [6].

Work on sorption and/or pillaring of inorganic guests was also directed for catalysis studies, such as selective syn-gas conversion over a Fe-Ru pillared bentonite. A micro-mesoporous catalyst was obtained by pillaring a natural bentonite with ruthenium doped iron oligomers. The catalyst showed, for reaction temperatures above 623 K, a good selectivity toward the production of light hydrocarbons with a high percentage of olefinic products [7].

Bentonite was also used as support material for nickel hydrogenation catalysts in which the active phase has been deposited by means of the precipitation method. Mass transport limitations resulting from reaction of linoleic acid at Ni sites between lamellae of bentonite leads to consecutive hydrogenation resulting in stearic acid [8]. Iron oxide pillared clay was prepared by interaction of bentonite with partially hydrolysed ferric chloride solution [9]. The product has an interlayer spacing of about 14.7 Å and retained its high surface area even after heating at 500 °C for 2 h. Al-B-Si composite pillared clay was prepared and its catalytic cracking properties for gasoline showed that the introduction of Si enhanced

the catalytic activity and gasoline yield on pillared clay [10].

Here we discuss our work on the transformations of textural and microstructure of bentonite to CTB and its calcined products, CCTBs. The samples are expected to have different properties compared to the precursor, and it is hoped that the properties of the resulting materials could be improved relative to its precursor, especially its surface-related property.

Materials and method

CTB was prepared by the addition of 2 g bentonite in 100 ml 2 % acetic acid solution. Prior to the addition, the bentonite was first dried at 110 °C in an oven to a constant weight and used in its dry form.

The flask containing bentonite-chitosan was shaken at 125 rpm at 75 °C for 5 days. Upon completion of the aging process, the sample was washed and centrifuged several times, dried in an oven at 120 °C, and kept in a sample bottle for further use and characterisation.

The calcined products of CTB (CCTBs) were prepared by heating CTB in a tubular electric furnace at various temperatures, 100-1000 °C for 5 hours under atmospheric condition. The samples were then kept in sample bottles and stored in a dessicator for further characterisations.

Powder X-ray diffraction (PXRD) patterns of the samples were obtained by using filtered CuK_α radiation in a Siemens D-500 diffractometer. Surface texture characterisation of the samples was carried out by nitrogen gas adsorption-desorption at 77K using Micromeritics ASAP 2000. The samples were previously degassed at 250 °C overnight. Specific total surface areas were calculated using the BET. (Brunauer, Emmett, Teller) equations.

Results and discussion

PXRD diffractograms

Figures 1 (a-c) show the PXRD patterns for bentonite, CTB and CCTBs. The diffractogram for CTB shows well-defined peak at 15.9 Å with high intensity. However for bentonite, a similar peak was observed with very low intensity and was not well defined, as shown in Figure 1a. This indicates that treatment of bentonite with chitosan solution resulting in better crystallinity of the resulting CTB.

On calcination of CTB to form CCTBs, it was found that the layered structure of bentonite remained

unchanged, even when the sample was calcined at 800 °C, as shown in Figures 1(b-c). However detailed

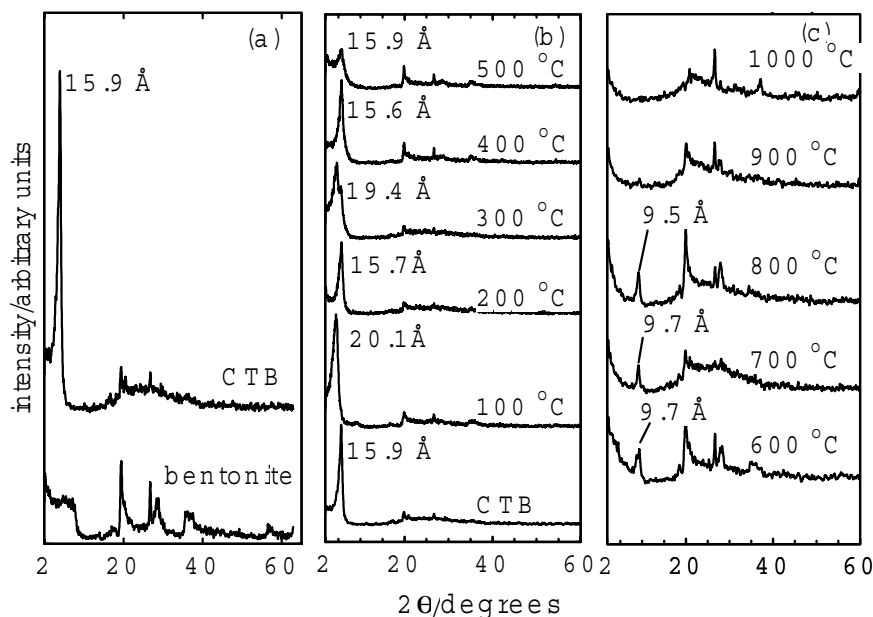


Figure 1 : PXRD patterns for bentonite and CTB (a), CCTBs prepared by calcination at 100-500 °C (b) and at 600-1000 °C (c).

Table 1 : Basal spacing and textural properties of chitosan, bentonite, CTB and CCTBs prepared at various temperatures 100-1000 °C.

	basal spacing (Å)	BET (m ² g ⁻¹)	micropore (m ² g ⁻¹)	micropore (%)	BJH (Å)
chitosan	-	0.3	-	-	100
bentonite	15.9	35	9	25.7	106
CTB	15.9	13	2	15.4	325
Calcination temperature (°C)	CCTBs				
100	20.1	14	0.3	2.1	107
200	15.7	13	1	7.7	111
300	19.4	18	1	5.6	99
400	15.6	36	11	30.6	91
500	15.9	45	15	33.3	84
600	9.5	38	9	23.7	82
700	9.7	28	3	10.7	89
800	9.7	17	2	11.8	110
900	-	6	0.9	15.0	160
1000	-	2	0.3	15.0	160

observation revealed that three stages occurred in the process. The first stage, from 100 to 500 °C, shows that the basal spacing of the samples fluctuated from 20.1 to 15.9 Å. In the second stage, from 600-800 °C, the basal spacing was reduced to around 9.6 Å and finally the layered structure collapsed at 900 °C. The

values of the basal spacing are given in Table 1. We believed that in the first stage, evaporation of surface and interlayer water took place during the calcination process, without disturbing the interlayer cations. However, this process was completed when the calcination process took place in the first stage. This

means that at higher temperature in the second stage, complete evaporation of water molecule in the interlayer, together with decomposition and/or expulsion of the intergallery cations such as carbonate took place, resulting in further reduction of the basal spacing to around 9.6 Å. Calcination at 900 °C, shows the formation of a new phase and the layered structure of bentonite has completely collapsed.

Adsorption-desorption isotherm

Figure 2 shows the adsorption-desorption isotherms for bentonite, CTB and CCTBs. Only isotherms for CCTBs calcined at 200, 400, 600, 800 and 1000 °C is presented in the figure.

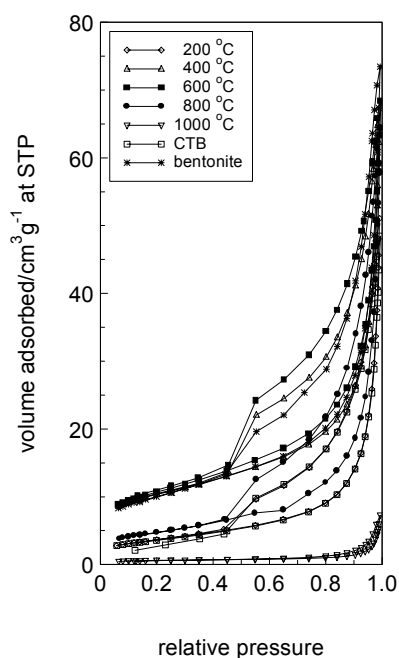


Figure 2 : The adsorption-desorption isotherms for bentonite, CTB and CCTBs calcined at various temperatures, 200-1000 °C.

As shown in the figure, the adsorption isotherm for all the samples is of Type IV [11], with adsorption increasing slowly at low relative pressure in the range of 0.0-0.9 with a small volume of gas uptake. Further increase of the relative pressure near to the saturated pressure (>0.9) resulted in a rapid uptake of the adsorbent on the adsorbates. This indicated a mesopore-rich texture of all the samples with low surface area.

The presence of the micropore component can be observed at low relative pressure, in agreement with the observation of a curve at around 0.0 to 0.1. In addition, the volume adsorbed is higher for bentonite,

and CCTBs calcined at 400 and 600 °C than to CTB and CCTBs calcined at 200 and 800 °C. The volume adsorbed is even lower for CCTB heated at 1000 °C. This is parallel with the trend of surface area-calcination temperature plot.

Pore size distribution

Figure 3 shows the pore size distribution for bentonite, CTB and CCTBs calcined at various temperatures, 200-1000 °C.

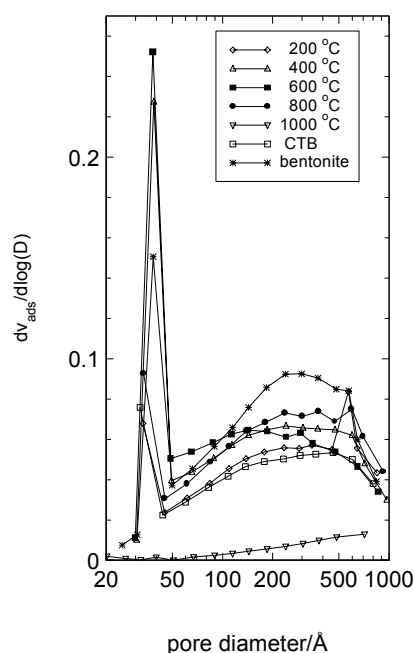


Figure 3 : The pore size distribution for bentonite, CTB and CCTBs calcined at various temperatures, 200-1000 °C.

As shown in the figure, the pore size distribution is dominated by 2 pore size distributions; a sharp high intensity peak centered at around 40 Å and a broad low intensity peak centered at around 300-400 Å.

The intensity of the pore size distribution at 40 Å is dominated by CCTBs calcined at 600 °C, followed by 400 °C, and bentonite. However, the pore size distribution shifted to at about 35 Å for CTB and CCTBs calcined at 200 and 800 °C. No well-defined pore size distribution was observed for CCTB calcined at 1000 °C.

As a result of the desorption isotherm, the average pore diameter by BJH desorption pore size distribution for bentonite, CTB and CCTBs is presented in Table 1. The average pore diameter for bentonite is 106 Å and increased to 325 Å as a result of chitosan treatment in the formation of CTB.

However, for CCTBs, the average pore diameter decreased to a minimum with a value of 82 Å when it was prepared by calcination at 600 °C, thereafter increased to 160 Å for both CCTBs calcined at 800 and 1000 °C.

The effect of calcination temperature on the surface area

BET and micropore surface area of the samples were determined, and given in Table 1. The BET and micropore surface area of bentonite is 35 and 9 m²/g, respectively, compared to 13 and 2 m²/g, for CTB respectively. This shows that as a result of chitosan treatment, bentonite surface area and its micropore component, decreased. A very low BET surface area of only 0.3 m²/g was obtained for chitosan.

Plot of BET surface area against calcination temperature for CCTBs is given in Figure 4. As shown in the figure, the BET surface area increased with temperature up to an optimum at 500 °C, thereafter decreased. The maximum surface area is 45 m²/g. A similar trend was also observed for micropore surface area, with a maximum value of 15 m²/g. This is equivalent to about 33 % contribution of micropore to the total surface area.

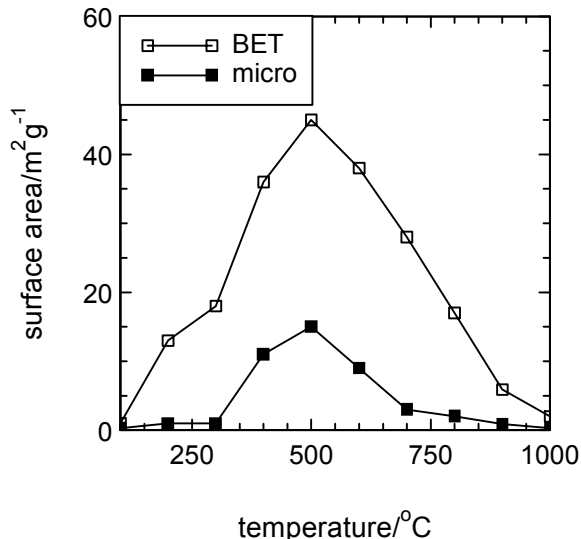
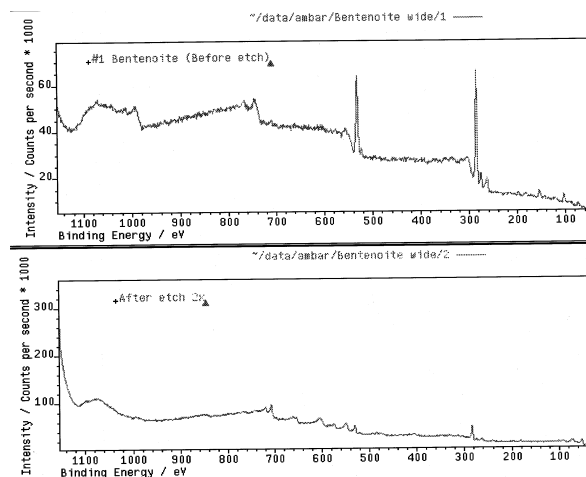


Figure 4 : The effect of surface area on the calcination temperature for CTB to produced CCTBs.

X-ray photoelectron study

Figures 5 a-b show the wide scan XPS for CTB and etched-CTB. Peak at 286 and 534 eV was assigned as C 1s and O 1s, respectively in CTB. The peak at 286 eV was almost completely diminished for the etched sample. However, the peak at 534 eV was still present

but with very low intensity. No peak belongs to nitrogen that can be observed in both CTB and the etched-CTB in the XPS spectra. This indicates that no chitosan was intercalated inside the interlayer of silicate.



Figures 5 : Wide scan XPS spectra for CTB (top) and etched-CTB (bottom).

Surface morphology

Figure 6 shows some typical surface morphology for CCTBs calcined at 200-1000 °C. All of them show an agglomerate of non porous structure and this structure was only transformed to a porous one when the calcination temperature reached 1000 °C.

Conclusion

Chitosan-treated bentonite can be prepared by using a 2 % chitosan in acetic acid solution. The resulting XRD pattern of CBT shows a sharper and higher intensity compared to the XRD pattern of the precursor, bentonite. CHNS analysis showed that CTB contains only 2.6 % carbon. This indicates that the intercalation of the chitosan into the bentonite layered silicate by direct intercalation did not take place, and probably chitosan was only adsorbed on the surface of the bentonite. XPS analysis indicated that no nitrogen could be detected in the etched CTB sample. This shows that chitosan was not intercalated in the silicate interlayer, and the increase of the XRD intensity was only due to a better crystallinity of CTB as a result of the treatment.

The texture and surface area of the CTB changed; the BET and micropore surface area decreased compared to the precursor, bentonite from 35 to 13 m²/g for BET, with 9 to 2 % contribution of micropore surface area. Calcination of CTB was done

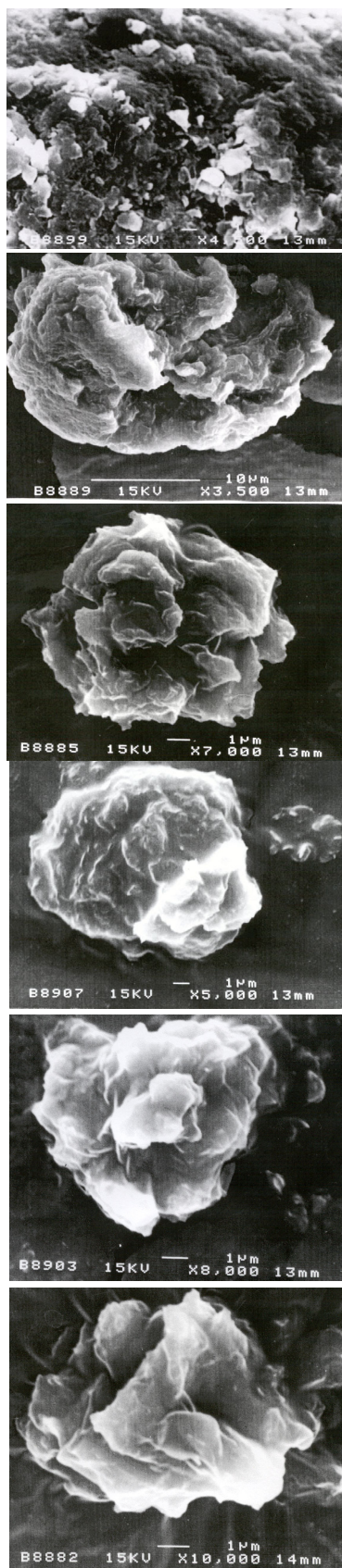


Figure 6: surface morphology for CTB and CCTBs calcined at 200, 400, 600, 800 and 1000 °C (from top to bottom).

at (100-1000) °C and resulted in an increase of BET and micropore surface area with calcination temperature, with an optimum at 500 °C (45 m²/g with 15% contribution of the micropore surface area). Thereafter, the surface area decreased with temperature. Surface morphology of CTB showed a non-porous agglomerate structure and this structure was changed to a porous one only when the sample was heated to 1000 °C.

Acknowledgement

The support of this research by the Universiti Putra Malaysia, under short term, Grant No. 50205-99-06 is gratefully acknowledged.

References

1. Q. Li, E.W. Grandmaison, M.F.A. Goosen and E.T. Dunn. 1992. Applications and Properties of Chitosan, *J. Bioactive and Compat. Poly.* 7: (4) 370-397.
2. R. E. Grim, 1962. *International Series in the Earth Science-Applied Clay Mineralogy.* McGraw-Hill Book Co. Inc., New York.
3. D. L. Jiang, Y.L. Weng and R.T. Tong, 1999. Preparation and characteristics of polyaniline/bentonite layered nanocomposites, *Acta Physico-Chimica Sinica* 15(1), 69-72.
4. D. C. Lee and L. W. Jang. 1998. Characterization of Epoxy-clay Hybrid Composite Prepared by Emulsion Polymerization, *J. Appl. Poly. Sci.* 68(12): 1997-2005.
5. T. Seckin, A. Gultek, Y. Onal, E. Yakinci and I. Aksoy, 1997. Synthesis, Characterization and Thermal Properties of Bentonite-polyacrylate Sol-gel Materials, *J. Mater. Chem.* 7(2): 265-269.
6. L. Popp, E. Toth, M. Toth, I. Paszli, V. Izvekov and M. Gabor, 1998. Synthesis and characterizations of hydroxy-aluminum cross-linked montmorillonite, *J. Thermal Anal. Calor.* 53(2), 585-596.
7. R. Ganzerla, M. Lenarda, L. Storaro and R. Bertinello. 1998. Selective Syn-gas Conversion over a Fe-Ru Pillared Bentonite, *Nat. Gas Conver. V.*, 119: 131-136.
8. J. A. Anderson, M.T. Rodrigo, L. Daza and S. Mendioroz. 1993. Influence of the Support in the Selectivity of Ni Clay Catalysts for Vegetable Oil Hydrogenation, *Langmuir*, 9 (10): 2485-2490.
9. H. M. Mody, P. M. Oza, V. P. Pandya. 1993. Thermally Stable and Acidic Iron-Oxide Pillared Clay, *J. Ind. Chem. Soc.* 70(1): 11-13.
10. W. Y. Xu, Y. H. Yao, X. M. Xie, S. H. Liu and J. P. Li. 1991, Preparation and Properties of Al-B-Si Composite Pillared Bentonite, *Reac. Kinetics Catal. Lett.* 44 (1): 115-120.
11. E. P. Barret, L. S. Joyner, and P. P. Halenda. 1951. *J. Am. Chem. Soc.* 73: 373-376.