Preparatıon And Characterızatıon Of Pıllared Clays

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Abstract Pillared clays are a new class of materials, in which large surface and pore volumes can be obtained according to the type of pillars. These solids have enormous potential for application in adsorption and catalytic processes. In the present study, two different pillared clays were studied. At first, alpha-sepiolite wastes were collected and Al-pillared sepiolite synthesis was carried out using these wastes. Another pillared clay (Al-pillared montmorillonite) was a commercial product. The morphology and surface functional groups of the materials have been analysed with the aid of x-ray diffraction (XRD) and Fourier Transform Infrared (FT-IR) spectroscopy. The specific surface area of the pillared clays was determined by nitrogen adsorption. The specific surface area of the pillared clays was determined by nitrogen adsorption using an automatic adsorption instrument. The BET surface area of pillared clays was determined by the application of the Brunauer-Emmett-Teller (BET) analysis, software available with instrument.

Keywords: Sepiolite; Montmorillonite; Pillared-clay; Waste utilization

INTRODUCTION

In recent years, material sciences have involved the studies related to the production of materials having a controlled pore structure and improvement of porous materials found in the nature. The production principle is to hold the inorganic layers a part from each other, introducing a bulky guest agent between them. When the used materials are clay minerals, the resulting materials after pillaring are called Pillared Layered Clays (PILCs). The host solid and the production conditions have rather important effects on the quality of the product. Due to its high cation exchange capacity, swelling properties, and large sheets, montmorillonite and sepiolite type clays have an important place in the production of pillared clays.

Pillared clays, a peculiar type of porous and high surface area solid material, have attracted considerable attention for application as catalysts, catalytic supports, and sorbents (Mokaya and Jones, 1995; Martínez-Ortiz *et al.*, 2003; Cseri *et al.*, 1995). They are prepared by intercalating polycations into the interlayer region of expandable clay materials. After calcination, the polycations were converted into robust metal oxide pillars, expanding the layers of the clay. The intercalated polycations increase the basal spacing of the clays and upon heating, are converted to metal oxide clusters by dehydration and dehydroxylation. As a result, a two dimensional porous network is generated. Pillared clays can be used for ion exchangers and ion-selective membranes, ultrafiltration and membranes, selective adsorption of gases, pollutant scavenging and waste management, sensors, acid catalysed organic reactions, non-acid catalysed organic reaction, photochemistry and photocatalysis, immobilization of enzymes, electrochemically active coatings, and protective coatings. Until now most of the research on pillared clays has been focussed on the Al_{13} polyoxocation (referred to as Keggin molecule, $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$) as a pillaring agent (Kloprogge, 1998; Kloprogge *et al.*, 2005; Manohar *et al.*, 2006). That's why Al_{13} polyoxocation was prefered in this study. Also, preparation procedure of this pillaring agent is relatively simple.

The most common smectite clay mineral is montmorillonite (MMT). MMT is evolved from volcanic ashes by weathering or hydrothermal effects like other aluminum-rich minerals and composed the highest part of the volcanic ash clay called as bentonite. The terminology of the word of bentonite can be summarized like that: The rock term bentonite which is commonly used for smectite group minerals (sodium montmorillonite, calcium montmorillonite, saponite (Mg), nontronite (Fe), and hectorite (Li)) as a clay material altered from a glassy igneous material, usually volcanic ash. (Murray, 2007). Each 2:1 layer of smectites has two silica tetrahedral (T) sheets bonded to a central alumina octahedral (O) sheet. Montmorillonite is a 2:1-type aluminosilicate. The net negative electric charge of the 2:1 layers arising from the isomorphous substitution of Al^{3+} with Fe^{2+} and Mg^{2+} in the octahedral sites and Si^{4+} with Al^{3+} in the tetrahedral sites, is balanced by hydrated exchangeable cations in the interlayers (mostly Ca^{2+} and Na^+) (Yener *et al.*, 2012; Tamayo and Kyziol-Komosinska, 2012). The ideal mineral formula for montmorillonite is $(Na, Ca)_{0.33}(Al_{1.67}, Mg_{0.33})Si_4O_{10}(OH)2 \cdot nH_2O$ (Grim,1968).

Sepiolite is a clay mineral with a wide range of industrial applications based on its physicochemical properties, especially its surface properties. The sepiolite is clay mineral which is a fibrous magnesium silicate of ideal formula $(Si_{12}O_{30}Mg_8(OH)_4(H_2O)_4.8H_2O)$. The mezopore size (an average of 37 A° ^{2}) of sepiolite is extremely interesting in this regard. Sepiolite belongs to the phyllosilicate group of clay minerals. It has peculiar surface properties and important industrial interest due to its high sorbing capacity (Alvarez *et al.*, 1984). Its structure is quite different from that of smectites. It

consists in the alteration of blocks and tunnels that grow up in the fiber direction (Santaren, *et al*., 1990). Each structure is built up of two tetrahedral silica sheets "in sandwich" with a central magnesia sheet in a way similar to that which occurs in other 2:1 silicates, although in sepiolite there is a discontinuity of the silica sheets that gives rise to those structural tunnels. This arrangement determines that silanol groups (Si–OH) are present at the border of each block at the external surface of the silicate. These silanol groups, together with the water molecules coordinated to the Mg ions at the borders of the structural blocks, are the main active centers for adsorption (Casal, *et al*. 2001). These characteristics of sepiolite make it a powerful sorbent for neutral organic molecules and organic cations (Alvarez *et al*., 1984). The dimensions of the cross section of sepiolite tunnels are about 11 x 4 $\mathring{A}^2$, which shelter two types of water molecules: (a) coordinated water molecules bonded to Mg^{2+} ions located at the edges of octahedral sheet, and (b) zeolitic water bonded to the coordinated water molecules through hydrogen bonding (Alvarez *et al*., 1984; Santaren, *et al*., 1990; Kuang *et al*., 2006).

The aim of the present research was to delevop for the incorporation of in the different kinds of clays structure in order to produce cheap and useful new porous materials. There are large deposits of these clays in Turkey (Balcı and Dinçel, 2002). This favorable combination of factors suggested that this bentonite and sepiolite could prove to be an economical source for artificially produced pillared layered clays. For these porpose, two different pillared clays were studied. At first, alpha-sepiolite wastes were collected and Al-pillared sepiolite synthesis was carried out using these wastes. Another pillared clay (Al pillared montmorillonite) was a commercial product. The structural properties of pillared clays were analyzed XRD, N_2-sorption, SEM and FTIR techniques.

2. MATERIALS AND METHODS

2.1. Materials Al-pillared montmorillonite was supplied by Sigma-Aldrich. The alpha-sepiolite was taken from the Eskişehir region (Turkey), was used as the starting material for the Al-pillared sepiolite synthesis. Because it was received as it was taken out of the ground, without having been processed, it contained many impurities. In order to purify it, a decantation and centrifugation process was applied. Following this process, clay had been dried in an oven at 90 °C and it was ground.

2.2. Preparation of Al-PILC The pillaring solution was prepared by titrating aqueous NaOH with aqueous $AlCl_3.6H_2O$. 400 ml of 0.1 M NaOH solution wad added dropwise to 200 mL of 0.1 M $AlCl_3$ solution at a rate of 1 ml min^{-1}. Dropping process took approximately 7 hours. Then the pillaring solution was stirred for 2 h at 60 °C and then aged overnight at room temperature. After aging, 500 ml of the pillaring solution was reacted with 10 g of aqueous suspension of purified sepiolite. The slurry was stirred at 60 °C for 2 h, then washed and centrifuged till the absence of chloride and oven-dried at 80 °C for 18 h and calcined at 400 °C for 2 h.

2.3. Characterization techniques X-ray diffraction (XRD) patterns were recorded between 1° and 20° (2θ) at a scanning speed of 2° min^{-1} using Rigaku Ultima-IV diffractometer with Cu Kα radiation (40kV/30mA).

Pillared clays were coated with 200 A of gold by Polaron SC7620 sputter coater and observed over a magnification range of 1000 to 5000. The FTIR spectra of the Al-pillared sepiolite and Al-pillared montmorillonite were recorded using a Perkin Elmer 100 Fourier-transformed infrared (FT-IR) spectrophotometer in the wave number range 4000-400 cm^{-1} using DRIFT (Diffuse Reflectance Infrared Fourier Transform) technique. Spectrums of the Al-pillared sepiolite and Al-pillared montmorillonite were obtained using KBr dilution, and finely powdered KBr was used as reference. Each sample spectrum was obtained by collecting 64 scans at a 4 cm^{-1} spectral resolution. The specific surface area of the pillared clays was determined by nitrogen adsorption at 77 K using an automatic adsorption instrument (Quantachrome, Autosorb-1C). The BET surface area of pillared clays was determined by the application of the Brunauer-Emmett-Teller (BET) analysis, software available with instrument. The BET surface areas were assesed by applying relative pressures ranging from 0.01 to 0.3.

3. RESULTS AND DISCUSSION

Much interest and research have, since 1970s, been directed toward the synthesis of pillared clays with higher thermal and hydrothermal stabilities. For these reasons later developments in the field were focused on the use of partially hydrolyzed metal cations as pillaring candidates. Thermal treatment of the intercalated oligomeric cations leads, following their dehydration and dehydroxylation, to metal oxide pillars characterized by enhanced thermal stability, large surface areas, sufficient acid sites and pores. Any metal oxide or salt that forms polynuclear species upon hydrolysis can be inserted as pillars, and all layered clays of the abundant phyllosilicate family as well as other layered clays can be used as the hosts (Brindley, 1977; Vaughan, *et al*., 1979; Farfan-Torres and Grange, 1990; Lahav, *et al*., 1978; Shabtai, 1984; Pinnavaia *et al*., 1984, Petridis, 1994; Pinnavaia, 1983).

The XRD patterns of the Al-pillared sepiolite and Al-pillared montmorillonite in the 2θ range of 1–20°. Pillaring of clays with Al is thought to be an ion exchange process of the major pillaring agent $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, the so called keggin or Al_{13} ions were able, through the XRD analysis, to confirm the intercalation of aluminum polycations Al_{13} with basal spacings of about 18 Å at room temperature. The sepiolite was identified by a strong d001 X-ray reflection 12 Å (Brindley and Brown, 1984). A strong diffraction peak near 2θ=7.2° can be seen. This is a characteristic peak of layered two-dimensional lattice structure minerals indicates that sepiolite is a kind of layered fibrous structure mineral similar to concentric circles (Tang *et al*., 2012). Therefore, structure and crystallinity of sepiolite were maintained after pillaring. The intensity of the diffraction peak of Al-pillared sepiolite is twice as high as Al-pillared montmorillonite. Diffraction peaks at 2θ=7.2° and 2θ=4.9° were indexed as (1 1 0) and (0 0 1) planes with basal spacing of 12.33 Å and 18.07 Å, respectively (Table 1). XRD analysis shows that the produced pillared layered clays is successful.

In BET measurements, 287.5 and 210.8 m^2 g^{-1} values were obtained for Al-pillared sepiolite and Al-pillared montmorillonite, respectively (Table 1). Montmorillonite and sepiolite both have high surface areas. In the case of

the montmorillonite, this property is due to the existence of an interlayer space (internal surface) commonly occupied by hydrated exchangeable cations, while in the sepiolite, it is caused by the presence of fibrous morphology and intra-crystalline tunnels (Legido *et al*., 2007; Galan, 1996). Some of the surface area data available are as follows: 286 m^2 g^{-1} (Al-pillared bentonite), 272 m^2 g^{-1} (Al-pillared montmorillonite), 320 m^2 g^{-1} (Al-pillared saponite), 288 m^2 g^{-1} (Fe-pillared sepiolite) (Jalil et, al, 2013; Gil *et al*., 2001; Moreno *et al*., 1997; Konstantinou *et al*., 2000; Akçay, 2004). According to Shuali *et al*., 2011 "the porosity spectrum of sepiolite is attributed to the contribution of two sources: a) External porosity resulting from the inter-fibres/bundles spaces and b) Structural porosity resulting from the repeated inversion of the silicate layer.

Table 1. XRD and BET data of pillared clays

Sample	2θ	d (Å)	Surface Area (m^2/g)
Al-pillared sepiolite	7.17	12.33	287.5
Al-pillared montmorillonite	4.89	18.07	210.8

Figure 1 shows the FTIR spectrum of Al-pillared sepiolite and Al-pillared montmorillonite. The parent montmorillonite showed two bands on the OH stretching region; a band at 3740 cm^{-1} attributable to silanol groups of the external layer and a broader band at 3650 cm^{-1} due to Al_2OH group of the octahedral layer. In the pillared samples, the intensity of the band at 3740 cm^{-1} increased with respect to the other. This can be interpreted as an effect of pillaring. The IR spectra in the fingerprint region were characterised by absorptions at 1200-1000 cm-1 (asymmetric stretching vibrations of SiO_4 tetrahedra), a doublet around 800 cm^{-1} (stretching vibrations of Al^{4+} tetrahedra) and absorptions at 526-471 cm^{-1} (bending Si-O vibrations). The decrease in intensity is due to the process of dehydration and dehydroxylation involved during pillaring. The process of pillaring substitutes a large amount of interlayer cations that generally exist in hydrated forms and thus decreases the intensity of –OH peaks. The aluminum pillaring agent had caused a decrease

in the free silica peak intensity which occurred at 840 and 916 cm^{-1} (Tomul and Balcı, 2007; Xue, *et al*., 2007).

In the FTIR spectra of Al-pillared sepiolite and Al-pillared montmorillonite, bands in the 4000–3000 cm^{-1} range corresponding to the vibrations of the Mg–OH group. The OH bending peak corresponding to the bound water is detected at 1652 and 1634 cm^{-1} for Al-pillared sepiolite and Al-pillared montmorillonite, respectively (Tunç, *et al*., 2012). Characteristic silicate bands were found between 1200–400 cm^{-1} and the bands at 504–430 cm^{-1} originated from Si-O bending and Al-O stretching vibration (Tomul and Balcı, 2007). The framework vibrations contain information about the structural characteristics of the material and their preservation after thermal treatments can be considered as a proof of the structural stability on pillaring.

4. CONCLUSION

The resultant pillared clays were characterized using FTIR, with a combination of XRD, SEM and textural analysis. The specific surface area of the pillared clays was determined by nitrogen adsorption. Results obtained from characterization techniques showed that there were changes in the clay structure with pillaring. The XRD patterns show that the basal spacings of the clays increase and it was observed that basal spacing, surface area values and the properties textural effects of clays were improved by pillaring.

In this study, two different pillared clays were studied. At first, alpha-sepiolite wastes were collected and Al-pillared sepiolite synthesis was carried out using these wastes. Another pillared clay (Al pillared montmorillonite) was a commercial product. In order to be able to better identify the nature of the pillared clay samples, analysis techniques, such as XRD, BET, and FTIR, were also applied. According to the XRD diffractograms of the Al-pillared sepiolite and as Al-pillared montmorillonite the characteristic basal space of Al-pillared sepiolite was calculated to be 12.33Å, while that of Al-pillared montmorillonite was 18.07Å. FTIR spectra of Al-pillared sepiolite and Al-pillared montmorillonite were compared. These fundamental data generated are of importance in developing clays can be used for industrial applications, especially heterogeneous catalysts and adsorbents.
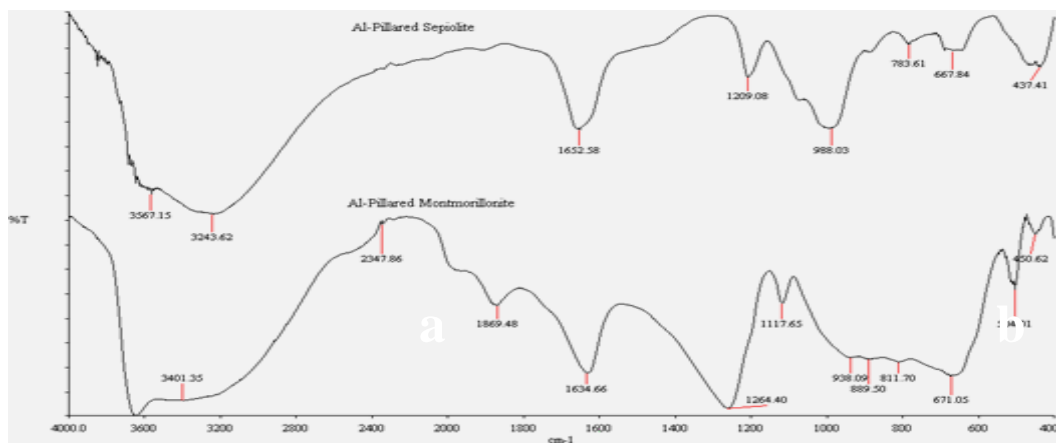
Figure 1. FTIR spectra of Al-pillared sepiolite and Al-pillared montmorillonite

References

Akçay, M., (2004), FT-IR spectroscopic investigation of the adsorption pyridine on the raw sepiolite and Fe-pillared sepiolite from Anatolia, Journal of Molecular Structure, **694**, 21-26.

Alvarez, A., (1984), Sepiolite: Properties and Uses, in: E. Galán (Ed.), in: Palygorskite–Sepiolite, Occurrences, Genesis and Uses, Dev. Sedimentol., vol. 37, Elsevier, Amsterdam [12] Santaren, J., Sanz, J., Ruiz-Hitzky, E., (1990), Structural fluorine in sepiolite, Clay Miner., **38**, 63-68.

Balcı, S., Dincel Y., (2002), Ammonium ion adsorption with sepiolite: use of transient uptake method, Chem. Eng. Process., **41**, 79–85.

Brindley, G.W., Sempels, R.E., (1977), Preparation And Properties Of Some Hydroxy-Aluminium Beidellites, Clay Minerals, **12**, 229-237.

Brindley, G.W., Brown, G., (1984), Crystal structures of clay minerals and their X-ray identification, Mineral. Soc., London,105.

Casal, B., Merino, J., Serratosa, J.M., Ruiz-Hitzky, E., (2001), Sepiolite-based materials for the photo- and thermal-stabilization of pesticides, Appl. Clay Sci., **18**, 245-254.

Cseri, T., Bekassy, S., Figueras, F., Rizner, S., (1995), Benzylation of aromatics on ion-exchanged clays, J. Mol. Catal. **98**, 101-107.

Farfan-Torres, E. M., Grange, P.,(1990) Pillared Clays, J. Chim. Phys., **87**, 1547-1560.

Galan, E., (1996), Properties and Applications Of Palygorskite-Sepiolite Clays, Clay Minerals, **31**, 443-453.

Gil, A., Vicente, M.A., Lambert, J.F., Gandia, L.M., (2001), Platinum catalysts supported on Al-pillared clays: Application to the catalytic combustion of acetone and methyl-ethyl-ketone, Catalysis Today, **68**, 41-51.

Grim, R.E., (1968), Clay Mineralogy, second ed., McGraw–Hill, New York, p.79.

Kuang, U., Facey, G.A., Detellier, C., (2006), Organo-mineral nanohybrids. Incorporation, coordination and structuration role of acetone molecules in the tunnels of sepiolite, Journal of Materials Chemistry, **12**, 179–185..

Kloprogge, J.T., (1998), Synthesis of smectites and porous pillared clay catalysts: A Review, Journal of Porous Materials, **5**, 5–41.

Kloprogge, J.T., Duong, L.V., Frost, R.L., (2005), A review of the synthesis and characterisation of pillared clays and related porous materials for cracking of vegetable oils to produce biofuels, Environmental Geology, **47**, 967–981.

Konstantinou, I.K., Albanis, T.A., Petrakis, D.E., Pomonis, P.J., (2000), Removal of herbicides from aqueous solutions by adsorption on Al-pillared clays, Fe-Al pillared clays and mesoporous alumina aluminum phosphates,Water Res., **34**, 3123–3136.

Lahav, N., Shani N., and Shabtai, J., (1978), Cross-Linked Smectites II. Flocculation And Microfabric Characteristics Of Hydroxy-Alumınum-Montmorillonite, Clays Clay Miner., **26**, 116-124.

Legido, J.L., Medina, C., Mourelle, M.L., Carreterob, M.I., Pozo, M., (2007), Comparative study of the cooling rates of bentonite, sepiolite and common clays for their use in pelotherapy, Applied Clay Science, **36**, 148–160.

Martínez-Ortiz, M.J., Fetter, G., Domínguez, J.M., Melo-Banda J.A., Ramos-Gómez, R., (2003), Catalytic hydrotreating of heavy vacuum gas oil on Al- and Ti-pillared clays prepared by conventional and microwave irradiation methods Microporous Mesoporous Mater., **58**, 73-80.

Manohar, D.M., Noeline, B.F., Anirudhan, T.S., (2006), Adsorption performance of Al-pillared bentonite clay for the removal of cobalt(II) from aqueous phase, Applied Clay Science, **31,** 194–206.

Mokaya, R., Jones, W., (1995), Pillared Clays and Pillared Acid-Activated Clays: A Comparative-Study of Physical, Acidic, and Catalytic Properties, J. Catal., **153,** 76-85.

Moreno, S., Gutierrez, E., Alvarez, A., Papayannakos, N.G. and Poncelet, G., (1997), Al-pillared clays: from lab syntheses to pilot scale production. Characterisation and catalytic properties. Applied Catalysis A: General, **165**, 103-114.

Murray H.H., (2007), Occurrences, processing and applica- tions of kaolins, bentonites, palygorskite-sepiolite, and common clays, developments in clay science, Applied clay mineralogy, Elsevier: Boston, 180 p.

Petridis, D., (1994), Pillared clays en Nanophase Materials: Synthesis-Properties-Applications (Eds.: G. C. Hadjipanayis and R. W. Siegel), NATO ASI Series **Vol. 260**, 747-756, Kluwer Academic, Dordrecht.

Pinnavaia T. J., Tzou M-S., Landau S. D. , Raythatha R. H., (1984), On the Pillaring and Delamination of Smectite Clay Catalysts by Polyoxo Cations of Aluminum, J. Mol. Catal., **27**, 195-212.

Pinnavaia, T. J., (1983), Intercalated Clay Catalysts, Science, **220,** 365-371.

Roca Jalil, M.E., Vieira, R., Azevedo, D., Baschini, M., Sapag, K., (2013), Improvement in the adsorption of thiabendazole by using aluminum pillared clays, Appl. Clay Sci., **71**, 55–63.

Shabtai, J., Rosell, M., and Tokarz, M., (1984), Cross-linked smectites. III. Synthesis and properties of hydroxy-alumihum hectorites and fluorhectorites, Clays & Clay Minerals, **32**, 99-107.

Shuali, U., Nir, S., Rytwo, G., (2011), Adsorption of surfactants, dyes and cationic herbicides on sepiolite and palygorskite: modifications, applications and modelling. In: Galan, E., Singer, A. (Eds.), Advances in the Crystal Chemistry of Sepiolite and Palygorskite. Developments in Palygorskite–Sepiolite 351–374.

Tang,Q., Wang,F., Tang, m., Liang,J., Ren, C., (2012), Study on Pore Distribution and Formation Rule of Sepiolite Mineral Nanomaterials, Journal of Nanomaterials, Volume **2012**, Article ID 382603, 6 pages.

Tamayo, A., Kyziol-Komosinska, J., Sanchez, M.J., Calejas P.,Rubio J.,Barba M.F., (2012), Characterization and properties of treated smectites, J. Eur. Ceram. Soc., **32**, 2831–2841.

Tomul F. and Balcı, S., (2007), Synthesis and Characterization of Al-Pillared Interlayered Bentonites, G.U. Journal of Science, **21**, 21–31.

Tunç, S., Duman O., Kancı, B., (2012), Rheological Measurements of Na-Bentonite and Sepiolite Particles in the Presence of Tetradecyltrimethylammonium Bromide, Sodium Tetradecyl Sulfonate and Brij 30 Surfactants, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 398, 37–47.

Vaughan D.E.W., Lussier R.J., Magee J.S. Jr., (1979), Pillared interlayered clay materials useful as catalysts and sorbents. U.S. Patent no. 4, 176090..

Xue, W., He, H., Zhu, J. and Yuan, P., (2007), FTIR Investigation of CTAB-Al-Montmorillonite Complexes. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, **67**, 1030-1036.

Yener, N., Bicer, C., Onal, M., Sarıkaya,Y., (2012), Simultaneous determination of cation exchange capacity and surface area of

acid activated bentonite powders by methyleneblue sorption, Appl.Surf. Sci., **258**, 2534–2539.