

Nano Sized Value-Added Product from Nagar Parker Kaolin

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Abstract: Kaolin is one of the most common mineral and is generally known as China clay, that has formed from the chemical weathering of rocks in hot and moist climates. The most crucial element in the raw kaolin is alumina (Al_2O_3). It is an important material, used in the metallurgical industries for the production of variety of ceramics, alloys and the catalyst such as zeolite which is utilize in petroleum processing side. In Pakistan various industries spend high cost on importing the gamma alumina from other countries. Synthesis of alumina from indigenous kaolin plays an important role in the economic development of Pakistan. The current work is concentrated on Synthesis of gamma alumina from Nagar Parker raw Kaolin that is available in abundance and is not yet realized effectively. The Nagar Parker kaolin was beneficiated, metakaolinized, dealuminated, crystallized and calcined to obtain the gamma alumina and characterized via XRF, XRD and SEM. The thermal treatment of $\text{Al}(\text{OH})_3$ was carried out at various temperature ranges i.e. 300, 600, and 900°C and the fully formed gamma alumina was obtained at the temperature of 900°C. The synthesis of gamma alumina is commercially feasible and substitute of conventional Bayer process. This method also provides an alternative of the ecological pollution generated via Bayer method.

Keywords: Gamma Alumina, Kaolin, Nano Material, Nagar Parker, Environmental Friendly

1. Introduction

The Kaolin or China clay is mostly found in white color. $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ is its chemical structure having chemical composition is (32.57% alumina + 54.81% silica + 12.62% and found further inert traces). In Pakistan there is town Nagar Parker of (Tharparkar) in that area we found cost effective significance deposits of kaolin. In 1961 the Geological Survey of Pakistan deposit was first who primary reported about Nagar Parker kaolin. During the period of 1976-79 broad survey were carried out by Pakistan Mineral Development Corporation (PMDC). The 3.634 million tons of kaolin reserves were expectable on the basis of huge figure of exploratory and drilling pits, bulk sampling, physical tests along with chemical analysis [1].

In Tharparkar there is a town name Nagar parker, in Sindh territory of Pakistan found in the corner of (S-E) direction at the 150 km of distance from mithi. About 777 km.sq of an area covered by Nagar parker and having distinctive locations where the authentic reserve of kaolin has been found and these locations are (Parodhoro, Northern Parodhoro, Dhedvero, Dhedvero Extension, Dungri, Karkhi, Moti-jo-Vandhio, Alonio-jo-Vandhio, Dhingano, Dhanida, Didwa[2].

The Main oxide element in kaolin is alumina (Al_2O_3). It has eight distinctive polymorphs, seven metastable forms (γ , δ , κ , ρ , η , θ and χ) as well as the thermally steady α . When Alumina occurs in above forms, stuff is mention as Al_2O_3 of gamma, Al_2O_3 of delta, Al_2O_3 of kappa, Al_2O_3 of theta and Al_2O_3 of alpha in that order. Individually within these transitions γ -alumina crucial Nano sized material which is utilized in the industries[3]. It is significant fabric, utilized

within in the industry of metallurgy used for generation of various porcelain and alloys[4]. It is also used as a highly potent processing material and as a catalyst in biofuel and cell-fuel processing. Al_2O_3 remains imperative catalyst backing for metal sustaining furthermore a very vital catalysts such as zeolite utilized in handling of petro-chemicals and petroleum [5] [6] [7] [8].

Hosseini et al.[9], has shown in his study, Production of γ - Al_2O_3 from Kaolin and also verified the structure of γ -alumina was confirmed by XRD and FTIR, he was also determined the mean particles size of γ -alumina by SEM to be 0.5 - 0.9 μm . Salahudeen et al.[10] Also worked on kaolin; he gets gamma alumina from kankara kaolin through synthesis process, and also presented the characterization of the product. Khodadadi et al.[11] The work has done by Ahmad Khodadadi Darban on alumina this study is about the Nano size Al_2O_3 powder synthesis from raw kaolin and he describes further its utilization for elimination of arsenite from the solutions of aqueous solution. George et al[12] worked on kaolin but the aim of his study is to investigate as much as manufacture of alumina from local Nigerian clay which are extremely abundant in Akoko land, South-western, Nigeria. His work reports a process for synthesis of alumina from Nigerian kaolinite clay. Bawa et al [13] examines the thermal effects on the surface properties of Gamma alumina synthesized from kankara kaolin. He examined that gamma alumina is good material for catalyst support and having a great worth to its surface properties.

Aliyu et al [14] investigated the positive natural structure of γ -alumina which was confirmed by XRD and its ultimate diffractogram parameters and SEM additionally

decide the cruel particles measure of γ -alumina was decided by SEM to be 3 – 9 μm .

The aim of our research to recover the value-added product from indigenous kaolin reserve. Gamma Alumina is the product of Kaolin. It has found that, Gamma Alumina is crucial element due to its applications and huge occurrence of kaolin in Pakistan. Synthesis of alumina from indigenous kaolin plays an important role in the economic development of Pakistan.

3. Methodology

3.1 Materials

Indigenous kaolin was accumulated from Nagarparker (Tharparkar) District in Sindh province of Pakistan; NaOH pellets along with saturated H_2SO_4 were bought.

3.2 Clay Benefication

With the help of jaw crusher raw kaolin was broken and ground. The clay was soaked using 1000g/4L ratio between clay and water, duration of settling is 24 h. After that blend was mixed with stirrer motor at 200 revolutions per minute for 60 minute and then filter after that clay is free from impurities then it is dewatered until a solid clay cake was obtained. At 200°C the cake was oven dried out for 6 hours then disc pulverizes. Therefore, the producing sample is referred as Beneficiated Kaolin.

3.3 Metakaolinization

In this step at 750°C the beneficiated clay was heated with the equipment name Nabertherm for 2hours. Therefore the producing sample was referred as Meta Kaolin.

3.4 De-Alumination

To achieve an alumina sulfate from Meta kaolin, it is dealuminated by utilizing 50 wt. % saturated H_2SO_4 acid, for the generation of $\text{Al}_2(\text{SO}_4)_3$ aluminum sulfate. To accomplish an effective 50 wt% of sulfuric acid 120gm of Meta kaolin was blended with 361cm^3 of deionizer water to generate a homogeneous mixture and then H_2SO_4 of 98wt% was added in this mixture, to effectively obtain 50wt% H_2SO_4 of acid, after that to avoid mud formation the mixture was shaken with intense force. Subsequently the mixture was left for 7 min to react except any involvement of heat. Later 100% volume of distilled water was added to mixture for quenched the reaction. The consequence product was permeating with the help of vacuum filtration and through this we get filtrate -aluminum sulfate $\text{Al}_2(\text{SO}_4)_3$.

3.5 Crystallization of Alumina

The obtained $\text{Al}_2(\text{SO}_4)_3$ was crystallize to produce $\text{Al}(\text{OH})_3$ aluminum hydroxide. For obtaining of $\text{Al}(\text{OH})_3$, 50 wt.% solution of (NaOH) was titrated opposed to the $\text{Al}_2(\text{SO}_4)_3$ solution at room temperature with constantly stirring ,till solution pH was rose to 9. Precipitated $\text{Al}(\text{OH})_3$ with distilled water was washed unless the sulfur was removed, by utilizing of vacuum filtration the slurry of alumina was filtered, afterward for 6 h at 110°C dried it. Therefore, the obtaining specimen is referred to as AL0.

3.6 Calcination

After the crystallization the obtained alumina slurry or $\text{Al}(\text{OH})_3$ was powder by crushing through mortar with pestle. Subsequently for 2 hour the grinding material was calcined with different temperatures through Nabertherm at 300, 600, and 900 Celsius. Therefore, achieving specimens are mentions as Al_2O_3 at 300, 600 and 900°C respectively.

3.7 X-ray Diffraction

XRD is equipment which is primarily used for the structural properties determination as well as the recognition of minerals in form of solid. In this research work the equipment named as the Bruker, D8 Advance diffractometer was used with radiation of $\text{Cu K}\alpha$ to record the diffraction spectra. The powder patterns of X-ray Diffraction with conditions: (2θ) of 10° to 80° , Cu -target, 35 kV, 35 mA, and speed of the scanning is $0.05^\circ/\text{sec}$ were recorded and data was disclosed in the plot between 2θ angle and diffraction peaks intensity. The peaks positions of diffraction were discriminate through the data of reference base and recognition of compounds diffraction could be achieved.

3.8 X-ray Fluorescence Spectrometer

This equipment is mostly operating to specify samples elemental composition in solid state especially powder form. In this work for the measurement of composition of kaolin samples and synthetic products XRF (Phillip, Magi X Pro) was used.

3.9 Scanning Electron Microscopy

SEM is use for examination of Morphology of the solid sample. The measurement was done via MODEL JSM-6380 LV Scanning Element Microscope and Sputter coater machine was also used for nonconductive material.

4. Results and Discussion

4.1 (XRF) X-ray Fluorescence

Table.1.XRF analysis for the kaolin along with different treatments steps.

Oxide (wt.%)	BK	MK	AL0	AL3	AL6	AL9
Al_2O_3	28.79	32.68	50.38	58.78	66.08	78.96
SiO_2	50.74	58.13	ND	ND	ND	ND
Na_2O	0.05	0.08	1.42	1.29	0.93	0.31
K_2O	0.06	0.06	0.04	ND	ND	ND
MgO	0.46	0.49	0.52	0.49	0.21	0.05
CaO	2.38	2.27	1.27	0.67	0.42	0.26
SO_3	N.D	ND	18.16	12.68	10.72	6.03
Fe_2O_3	0.66	1.34	2.39	1.96	1.02	0.49
CL	0.29	0.12	0.26	0.39	0.21	0.01
LOI	16.37	4.47	25.16	23.74	20.41	13.62

ND: not determined.

The beneficiated kaolin of Nagar parker was primarily contained Alumina as well as Silica be composed 28.79 and 50.74 % respectively. The obtained ratio of Al/Si was 1.76%. It revealed from the XRF results that the kaolin contains various impurities such as iron, calcium, magnesium, sulfur trioxide, sodium oxide, potassium oxide and other trace elements. In addition, calcinated beneficiated kaolin, the Al and Si content was 32.68 and 58.13 % respectively, and the ratio of alumina/silica was 1.78, which showed a significant increment in the Al/Si ratio. After the de-alumination and precipitation process, the obtained Al(OH)₃ was composed of Al, and sulfur trioxide, but the Si content was not detected. This showed that de-alumination had separated the Silica particles into alumina component filtrate. In the Al(OH)₃ various impurities were still detected such as Iron (Fe₂O₃), calcium oxide (CaO) and disodium trioxide (Na₂O₃) consisting of 2.39, 1.27 and 1.42 % respectively. It was noted that a new impurity, Sulfur trioxide (SO₃) was detected in significant amount of 17.96% due to the use of H₂SO₄ during the process of de-alumination. The Al(OH)₃ was calcinated at various temperature ranges like 300, 600, and 900°C. The temperature range between 300 and 600°C, the raise of Al₂O₃ content in Al(OH)₃ was averaging 21% and SO₃ content had reduced on average by 30% and also the potassium (K₂O) was not detected at this stage. Furthermore, at 900 celcius material have successfully altered in to γ- Al₂O₃, having Al₂O₃ content was 78.96%. The significant increment of 51.2% was observed in the alumina content of initial Al(OH)₃. The reduction in the SO₃ content was up to 6.03 wt.%. It is observed that the starting Al(OH)₃ consisted high amount of SO₃ which decreased continuously with the increase of temperature. It is noted that at the temperature of 900°C, the SO₃ content continuously reduced and became negligible and Gamma alumina content continuously increased.

2.2 X-ray Diffraction

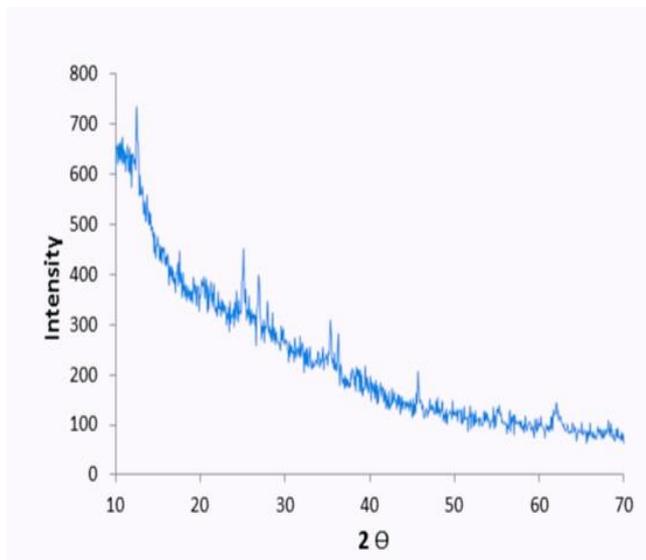


Figure.1.XRD pattern of beneficiated kaolin

The X-ray diffraction result of beneficiated showed in **Figure.1**. The pattern of X-ray diffraction of the B.K displayed all the kaolinite peaks, these peaks could be spot at Bragg's angles of 12.52, 17.56, 25.12, 26.87, 35.34, 36.32, 45.7, and 62.01°. However, at the angles of 26.87°,

and 17.56° the peaks were generated due to the presence of crystalline silica mica montmorillonite.

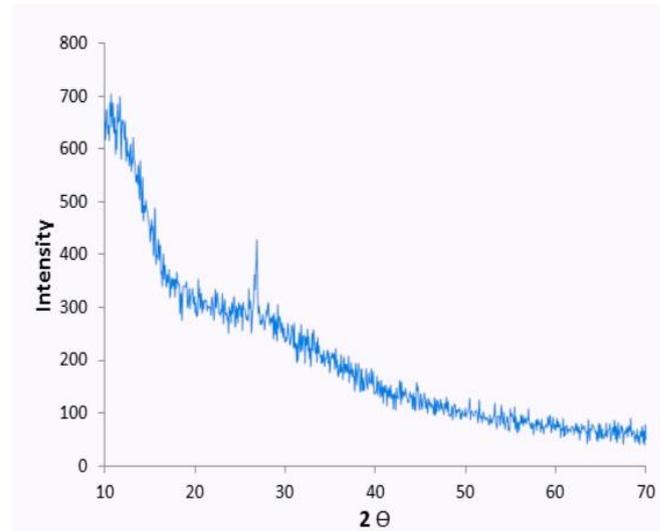


Figure.2.XRD pattern of Meta kaolin

It revealed from the XRD pattern of Meta kaolin that the material was highly amorphous. As a result of calcination, the crystalline structure of indigenous kaolinite crumbled and became amorphous Meta kaolin as shown in **Figure.2**. After metakaolinization only silica peak was observed in the XRD pattern. This result is consistent with salahudeen et al.

The XRD analysis of precipitated Al (OH)₃ attained prior to calcination Figure.3 indicates that aluminum hydroxide was (formless) amorphous, and the material seemed like gibbsite, aluminum hydroxide. Furthermore, the characteristics peaks of gibbsite, aluminum hydroxide was observed in the material at the angles of 20.41, 36.71 and 37.73°. However, the XRD analysis of precipitated Al (OH)₃ at the calcination of 300°C, the Al (OH)₃ was slightly changed, when compared with the non-calcinated Al (OH)₃ as shown in Figure. 3. Moreover, at 600°C calcination, a clear transformation in XRD result could be observed, the transformation in form trend had started to progress at the temperature of 600°C, the γ-Al₂O₃ peaks at 46 and 66° angles had begun showing the trend of becoming pronounced. The XRD analysis exhibited the complete transformation of Al(OH)₃ into γ-Al₂O₃ at 900°C. All the peaks for γ Al₂O₃ became obvious in the material at the angles of 36, 46 and 66°. Comparing with the XRD results of salahudeen et al.

The nano size Gamma alumina was 18.67nm quantified by Sherrer's equation which is also known as Debbay Scherrer equation as follows:

$$D = \frac{K \lambda}{(B \cos \theta)} \tag{1}$$

Where

D- Size of crystals in nm

λ - Wavelength of X-ray. For Mini XRD, Cu Kα average 1.54178 Å

K - Scherrer constant. K = 0.94 for spherical crystallites with cubic symmetry

B-is the FWHMs (Full Width at Half Maximum) observed for the sample
 θ – For Bragg’s angle.

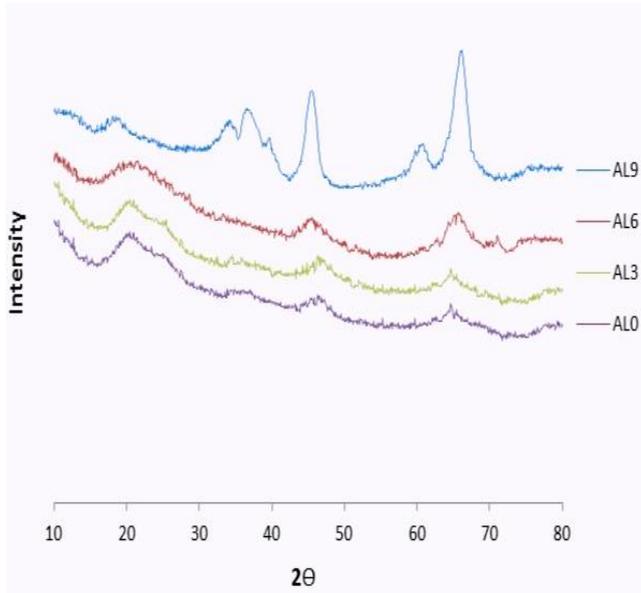


Figure.3.X-ray diffraction patterns for the Al (OH)₃ and different stages of calcinations.

3.3 Scanning Electron Microscope

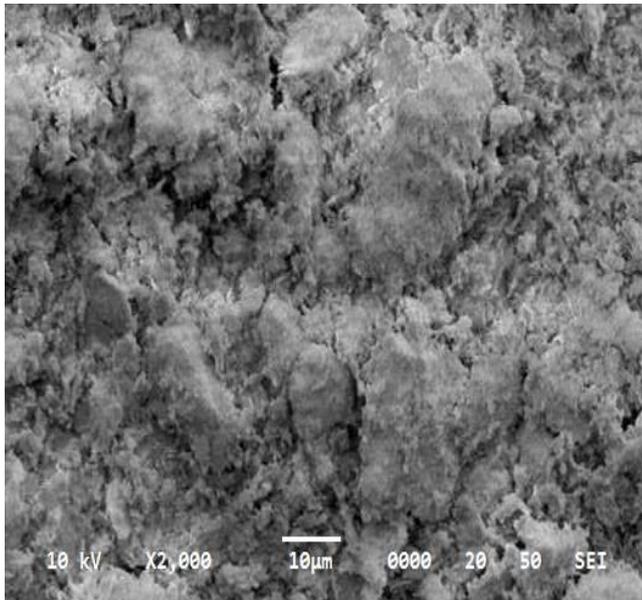


Figure.4.SEM image for the beneficiated kaolin

The Nagar parker beneficiated kaolin image is shown in **figure.4**. All the images were captured at the electron energy of 10 kV at the magnification of 2000. The structure of the beneficiated kaolin sample possesses the intermediate as well as large size of pores and identified by its loosely rounded packed surface morphology.

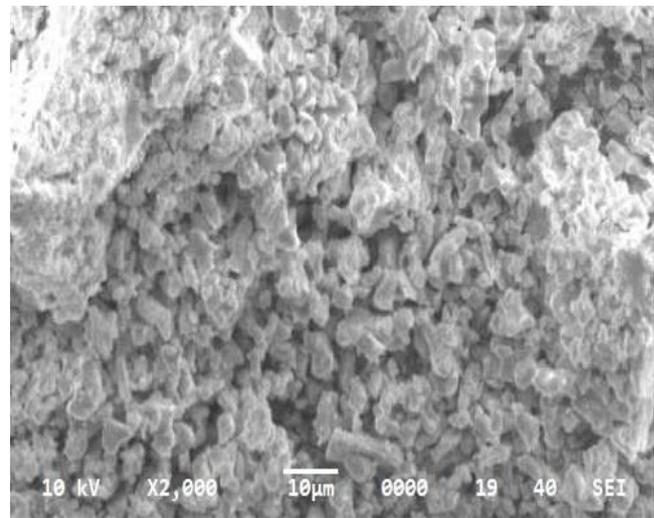


Figure.5.SEM images for the Al₂O₃at 900°C

Figure.5. showed the image of Al₂O₃ calcinated at 900°C. The morphology of the Al₂O₃ appeared completely different, and macro crystallites was closely compacted forming enormous lumps of flake like structures. It revealed from the Al₂O₃ image that the size of micro-crystallite was within the range of Nanometer. Consequently, the material was crystalline as was already analyzed via XRD technique as shown in Figure.3.

5. Conclusion

The gamma alumina was successfully synthesized obtained from the raw kaolin of Nagar parker by using novel technique. It reveled from the results that this method is commercially feasible and substitutes of the Bayer process. This process also provided a solution of the ecological pollution generated via conventional Bayer method. The Aluminum hydroxide Al (OH)₃ was calcinated at the various temperature ranges i.e. 300, 600 and 900 °C. The crystalline gamma alumina was successfully produced from Al(OH)₃ at the 900 °C. when we were compared the characterization of the gamma alumina obtained with the research paper of salahudeen et al (2015) indicated a great close of correlations. The Al₂O₃ content in synthesized γ-Al₂O₃ was 78.96 wt. %.

The estimation of synthesized crystal size of gamma alumina is 18.67 nm while. The researcher estimated crystal size of gamma alumina was 10 nano meters; therefore, the sizes of both materials were Nano and micro porous γ-Al₂O₃.

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