High Purity Alumina and Zeolite from Local Low Grade Kaolin

Meor Yusoff M.S.*, Masliana Muslim, Choo Tye Foo and Julie Andrianny Murshidi

Materials Technology Group,
Industrial Technology Division,
Malaysian Institute for Nuclear Technology Research, Bangi, 43000 Kajang, Selangor, Malaysia.

Abstract

Malaysia mainly produced low quality kaolin and the paper describes the development of a process to produce high purity alumina and zeolite from this mineral. Selective leaching technique was applied to remove 45% of the Al_2O_3 content in kaolin. The high purity alumina produced shows similar characteristic to the commercial product. An alkaline fusion stage was then carried to transform the kaolin mineral into zeolite. Identification of the crystalline phase by XRD shows that it consists of both zeolite P and hydroxysodalite. This was also confirmed by the FTIR technique.

Keywords: Alumina, zeolite, local grade kaolin

1.0   Introduction

Kaolin is a soft, white plastic clay consisting mainly of the mineral kaolinite, which is a hydrated aluminum silicate $Al_2Si_2O_5(OH)_4$. It is formed by the alteration of feldspar and muscovite. It is an important industrial mineral, which is used in many industrial applications. Malaysia produced 286,648 tons of kaolin in 2001 mainly from mines in Johor and Perak [1]. In Perak, which accounted for 83% of the total kaolin production, most kaolin mines operated are in the Bidor and the Tapah areas. However, locally produced kaolin is of low quality and mainly used in the ceramic sector.

Traditionally alumina is produced from bauxite via the Bayer's process [2]. Besides the majority of alumina is produced as smelting grade alumina for the production of aluminum metal, about 10% of the world's production is also produced as technical ceramic for high technology applications. Alumina is widely used as an advanced ceramic material due to its combination of physical, chemical and electrical properties. Its hardness and strength with good wear and chemical resistant at a very high temperature has made it a good choice for critical structural applications. The demand for alumina mainly comes from the electrical and electronic sectors due to its excellent dielectric and insulating properties. High purity alumina that is used for high technical applications are required to be of more than 95% purity with very low sodium and iron content. In the traditional processing method, the sodium impurity mainly comes from the used of sodium hydroxide whilst iron is present in the bauxite mineral [2].

Zeolite can also be produced synthetically and there are more than 150 synthetic zeolites that had been produced [3]. It was not until the 1930s and 1940s that scientists started to synthesize zeolites. Since then, hundreds of zeolites have been synthesized. Many of zeolite

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* Corresponding author: E-mail: meor@mint.gov.my

properties, such as structure, Si / Al ratio and pore size are determined by the synthesis parameters. Some of the variables that affect the type of zeolite formed by a particular synthetic procedure are: temperature, pH, crystallization time, gel composition, sources of reagents and order of mixing.

Presently synthetic zeolite is used more predominantly capturing about 82% of the total zeolite market. Amongst the major applications of synthetic zeolites are detergent builders, adsorption and separations and also catalysts. Catalysts represent the largest market for zeolites with more than a half billion-dollar market in the U.S. Such a large number is not surprising when one considers that the economics of zeolite catalysts in cracking processes alone have been estimated to be between \$1 and \$10 billion per year. The second largest U.S. market for synthetic zeolites (at about 350,000 tons/year) is the detergent powder industry, where zeolites provide an environmentally acceptable alternative to phosphates detergents. The price of zeolite also tends to vary between natural, synthetic and their applications. Natural zeolite cost about RM200-600/ton, detergent grade synthetic zeolite cost RM1, 900-2, 300/ton whilst catalyst grade synthetic zeolite are priced at USD 45,000/ton [4].

2.0   Materials & Method

Kaolin powder was first screened to particles below 75 μm in size and calcined at 800^0C for 3 hours in an electric furnace to loosen the alumina components [5]. Then, 18 g of the calcined sample was added with 600mL of a 1-3M sulfuric acid (H_2SO_4) solution in a flask fitted with a thermometer. The mixture of the sample and acid was heated to a temperature of 50^0–100^0C and then maintained at that temperature range for 240 min and stirred with a magnetic stirrer. After the mixture of the sample and acid had been leached, it was cooled to room temperature and filtered to remove the leach residue, which mainly consisted of silica. The filtered leach liquor was then added dropwise into 1000mL of ethanol again under stirring with a magnetic stirrer. Ethanol was used as a precipitating agent because Al^{3+} ions can be extracted from ethanol with high selectivity. The precipitates were washed again with the ethanol, and then dried at 100^0C for 6 hours. Finally, the precipitates were calcined at 1000^0C for 1 hour in an electrical furnace.

The kaolin powder was oven-dried at 120°C overnight. Then 20 g of dried kaolin was diluted in 250 ml of 2M H_2SO_4. The mixture was stirred with a magnetic stirrer and allowed to react for 4 hours at 80°C. At the end of the process, the solid was separated by filtration and then dried overnight at 80°C. The dried solid was mixed with 24 g of NaOH (ratio: 1 to 1.2). The mixture was then ball milled at 300 rpm for 30 minutes to obtain a homogenous fusion of solid. The solid is later calcined at fusion temperature of 550°C for 20 minutes. The calcined material was then mixed with 150 ml of distilled water, cured (stirred at room temperatured) for 24 hour, reflux at 100°C for 3 hours and filtered with 10 times washing with distilled water and oven-dried at 80°C overnight.

XRD (X-Ray Diffraction) technique was used to identify crystalline phase in the sample. The surface properties of kaolin and synthesized zeolites were characterized using Nitrogen uptake (BET surface area) using AUTOSORB-1 (Quantachrome Corporation). For morphological structure and identification of the powder size, samples were analyzed using SEM and Particle Size Analyzer. FTIR was used to illustrate the formation of zeolite.

3.0   Results and Discussion

3.1   Production of alumina (Al_2O_3)

Chemical analysis of the kaolin sample used for this study shows that it contains 60.95% of SiO_2 and 25.30% of Al_2O_3 with a Si/Al ratio of 2.4. The Si/Al ratio for zeolite ranges from 2.0 to 7.5 with the highly absorbing synthetic zeolite falls in the higher ratio. The Al_2O_3 content in kaolin was reduced by using a selective leaching technique. Here the SiO_2 content will relatively not be affected during this process.

The efficiency of alumina leaching can be illustrated by the degree of alumina extracted within the synthesized precipitates versus the amount of alumina in the starting kaolin. Degree of Al_2O_3 extraction was calculated by the following equation, Equation 1[5].

$$\text{Degree of } Al_2O_3 \text{ extraction} = \frac{[C] \times [D]}{[A] \times [B]} \times 100\% \tag{1}$$

A = weight of starting kaolin
B = concentration of Al_2O_3 in starting kaolin
C = weight of calcined precipitate
D = concentration of Al_2O_3 calcined precipitate

Dilute sulphuric acid was used in this leaching process to minimize the dissolution of other elements present in the local kaolin. Besides acid concentration, temperature is an important parameter in this process. The ease of extracting alumina from kaolin under acid treatment was investigated by comparing the different leaching temperatures used in the extraction. Figure 1 shows the effect of increased in leaching temperature to the degree of alumina extracted. In this study the range of leaching temperature used was from 50^0 to 100^0C using a 2M H_2SO_4 for 240 minutes.

As can be seen from Figure 2, the degree of alumina extraction recorded using a leaching temperature of 50^oC is very low, which is only 8%. However when the leaching temperature was increased to 60^oC, the degree of extraction increases drastically to 29%. Further increase in the leaching temperature to 80^oC, resulted in a higher degree of extraction of 40%. For the kaolin leaching process this is the optimum temperature for the recovery of Al_2O_3 as any further increase in the temperature will not improve the degree of alumina extraction value.

Another factor that could affect the degree of extraction is the leaching time. As the leaching time is increased more alumina can be extracted if other parameters are kept constant. Figure 2 shows the degree of alumina extraction as a function of leaching time. In this study the time is varied from 30 to 360 min using 2M H_2SO_4 and at a leaching temperature of 80^0C. The graph shows that for the first 30 minutes of leaching, 12% degree of extraction was obtained. This value increases rapidly to 22% when the leaching time is increased to 60 minutes. The degree of alumina extraction increases with the corresponding increase in leaching time until it reaches the optimum value of 45% for 240 minutes of leaching.
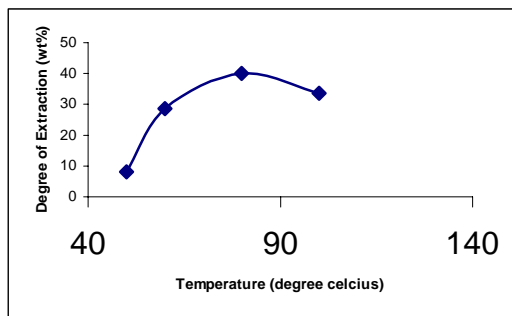
Figure 1   Graph of leaching temperature against degree of alumina extraction
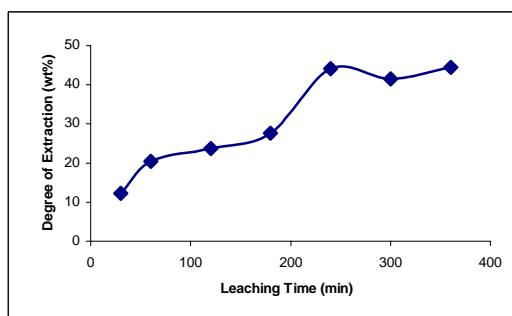

Figure 2   Graph of leaching time against degree of alumina extraction

Aluminum hydroxide was then precipitated from the leached solution by using propanol as the precipitating agent. After undergoing thermal treatment, the extract from this process was then characterized for its quality. Table 1 summarized the properties of alumina product in comparison with high purity commercial grade alumina.

Table 1 Properties of high purity alumina product in comparison with commercial product

Physical characteristics (Technique)	MINT's alumina	Commercial product [6]
Alumina crystalline phase (XRD)	α and γ single phases	α and γ single phases
Morphology (SEM)	α = rounded crystals γ = plates	α – rounded crystals γ – plates
Surface area (BET)	α = 20 m²/g γ = 85 m²/g	α = 3 - 20 m²/g γ = 60 - 85 m²/g
Median particle size, d_{50}	2.87 – 7.53 μm	0.4 - 55μm
Chemical characteristics		
Al_2O_3	97.5%	94 - 99.9%
Na_2O	Not detectable	0.05 – 0.50%
SiO_2	Not detectable	0.015 – 0.03%
Fe_2O_3	0.02%	0.025 – 0.50%
MnO	0.015%	Not detectable
Sulphur	0.20%	Not detectable

3.2   Production of zeolite

Kaolin possesses the Si-O or Al-O octahedral and tetrahedral structures respectively. Unfortunately, these Si-O and Al-O structures are inactive to modification or activation. This means that it is difficult to synthesize zeolites directly, and therefore kaolin must be pre-activated to change this inert structure [7]. The most effective way to activate such natural clay is to thermally transform the inert phase into the active phase at elevated temperatures in the presence of alkali hydroxide. Thus in this process a fusion hydrothermal process was used. In the fusion process, kaolin is thermally activated by the addition of NaOH to form an active Al and Si species. These species tend to react with each other and reconstruct to form ring-like structures that are the basic units for zeolite construction.

Figure 3 below shows the SEM micrograph of the zeolite sample synthesized from local kaolin. The morphology of this zeolite sample shows the presence of two different structures. First is the major agglomerated ring-like structure while the second is the minor plate structure.
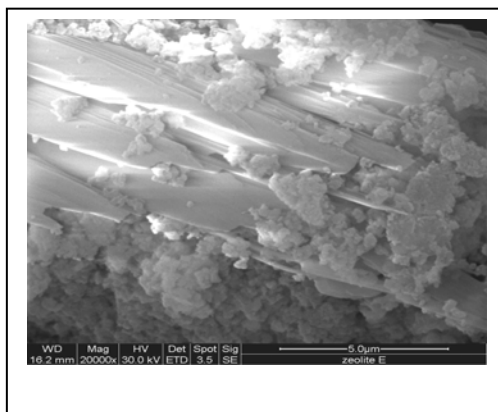

Figure 3   SEM micrograph of Zeolite

The product was then identified for the presence of crystalline phases by using the XRD technique (Figure 4). Sharp peaks of the product indicate that it is a crystalline material. On analysis of the peaks from this diffractogram it can be concluded that the major phase belongs to Zeolite P, $Na_6 Al_6 Si_{10} O_{32} . 12H_2O$ (JCPDS card 39-0219). Zeolite P exists in both high and low silica forms [3], where in the latter both cubic and tetragonal structures are present. The XRD diffractogram also shows the presence of another minor crystalline phase known as hydroxysodalite, $4Na_2O. 3Al_2O_3 . 6SiO_2 . H_2O$ (JCPDS card 11-401). As shown by previous researchers, this phase is attributed to the formation of an intermediate phase between kaolin and zeolite [3, 4 & 8]. Its formation may be resulted from the incomplete interaction of the aluminum and silicon species in the kaolin into the mixed aluminum and silicon ring-like structure found in zeolite. The presence of the hydroxysodalite phase can also be observed from the plate structure found in the SEM micrograph shown in Figure 1.

Another characteristic test performed is the FTIR technique. FTIR spectrum could indicate the existence of zeolite frameworks [8]. Here, a comparison was performed on the zeolite product (Figure 5a) and the kaolin sample (Figure 5b). The band formed at 3450 cm^{-1} on the zeolite product attests to the attachment of hydroxyl groups to the zeolitic framework. The

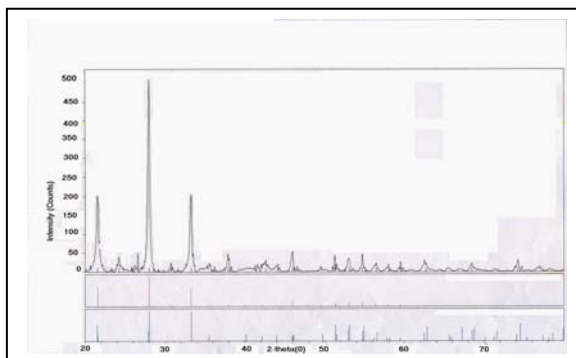1640 cm^{-1} band indicates the presence of adsorbed water on zeolite, a typical deformation band.

Figure 4   XRD diffractogram of Zeolite

The band at about 1000 cm^{-1} is probably due to internal tetrahedral zeolite structure vibration of asymmetrical stretch (n_{asym}), whereas the band at 1090 cm^{-1} is caused by asymmetrical stretch of external linkages. The band is conceived by the internal tetrahedral vibration band and identified by the slight deviation of the band line at higher wave number (after 1090 cm^{-1}). The bands at the range of 720-650 cm^{-1} show the symmetrical stretch vibrations of the internal tetrahedral structure whereas the bands at 650-500 cm^{-1} show the vibration of the double ring of external linkages. A relatively weak band in the region of 1400-1500 cm^{-1} is probably due to vibrations near non-zeolitic phases, those that are not converted to zeolite. In this case this is contributed from the hydroxysodalite phase.
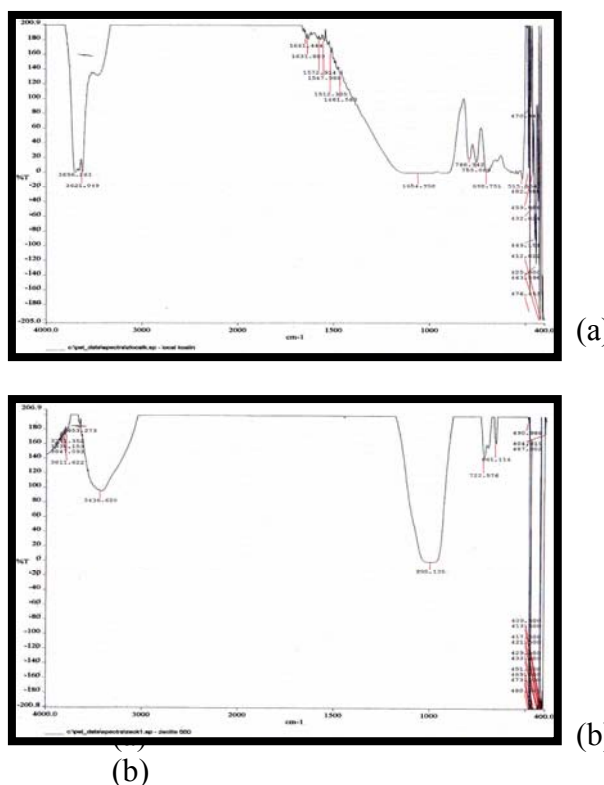

(a)

(b)

Figure 5   (a) FTIR spectra of Local Kaolin and (b) FTIR spectra of Zeolite

Particle size and surface area play an important role in determining the quality of zeolite product produced by the hydrothermal fusion process. The effect of this process on the particle size of zeolite can be seen in Figure 7. Results from the particle size analyzer shows the median particle size (d_{50}) of 4.462μm for zeolite with majority are in the 2.75–5.5 μm range. Another characteristic of the zeolite product that was studied is the surface area. Bigger surface area will result in a better absorption performance of the zeolite during the absorption process [9]. Results from the BET surface area analyzer shows that the zeolite product has a value of 34.3 m^2/g, which is more than three times the surface area value of untreated kaolin (10.6 m^2/g).
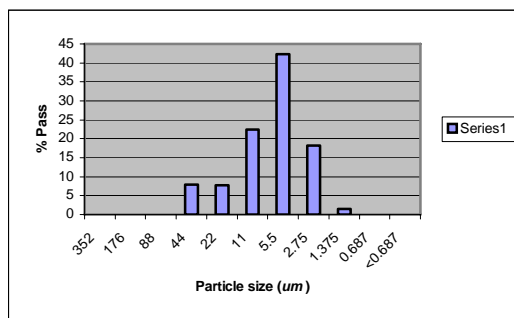

Figure 7   Particle size of Zeolite

4.0   Conclusion

This study shows the development of a hydrothermal process to produce two advanced ceramic products from Malaysian low quality kaolin. By using suitable selective leaching technique, a high purity alumina product that is comparable to that in the market can be produced. Zeolite P can also be produced by using the same process. The zeolite P produced from this process also shown to have better properties compared to that of local kaolin.

Acknowledgement

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