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PREPARATION OF MESO POROUS SILICA FROM BENTONITE BY ULTRAFINE GRINDING AND SELECTIVE LEACHING

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ABSTRACT

Preparation of meso porous silica from bentonite had been conducted by ultrafine grinding and leaching. The bentonite was taken from Nanggung, Bogor, West Java; it contains montmorillonite with porous structure. The ultrafine grinding was carried out using planetary ball mill (PBM) in wet condition (wet milling) in methanol. Optimum milling time was reached in 30 hours and it produced 77.4 nm of particle size. The process was continued with selective leaching in sulphuric acid solution to increase the amount of SiO_2 *from 54.13% to 86.21%, which decreased* Al_2O_3 *and* Fe_2O_3 *content gradually from 23.09% and 7.33% to 4.96% and 0.89% respectively. The leaching process produced porous silica material with pore size 6.5 nm (meso porous); 278* m^2/g *of surface area and 0.75 mL/g of pore volume.*

Keywords: meso porous silica, bentonite, ultrafine grinding, selective leaching

INTRODUCTION

Porous material in nanometer scale has been concerned by researcher and businessman because of its special characteristic to be used in various applications of industry. Well known applications of porous material are adsorbent, filter, and catalyst, while developing applications are being conducted for hydrogen storage in fuel cell technology and waste treatment (Zabukovec and Kauèiè, 2006).

Porous material is divided into 3 types based on its sizes, which are micro porous (< 2 nm), meso porous (2 - 50 nm), and macro porous (> 50 nm). Micro pore materials were recently started to be omitted by industry because of its limitation, such as the application of catalyst for crude oil hydro cracking, the pore is too small so the heavy fraction from crude oil can not transported through the pore (Darmawan, 2004). Therefore, meso porous material with bigger pores size is developing nowadays. One of meso porous materials which is commonly used in crude oil processing is M41S (founded by Mobil oil), which is known as synthetic zeolite (Kresge et.al.,1992). The production of it requires expensive organic compound and sensitive reaction condition, so the use of the material in large amount is rather difficult.

Aluminium silicate material has layer structure and could be easy to be modified, so it can be used as raw material of porous material preparation. Pillarisation is one of the technology to enlarge the pores of aluminium silicate material. Based on its layer structure, the material can be classified into 3 types, which are 1:1, 1:2, and 2:1. Generally, porous material is produced from 1:1 and 2:1 type. By considering the enormous reserves of bentonite, the material is to be highly potential source for porous material.

The preparation of porous material from aluminium silicate by ultrafine grinding and leaching affects crystal structure destruction and metal ions separation, which enlarge the pores of material. Few examples of porous material made by the method are kaolinite (Okada, 2005) and chrysotile (Suquet, 1989), which can produce various surfaces area about 20 to 670 m^2/g. The method, however, has rarely applied for bentonite clay especially on production of porous material and observation the

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leaching kinetics process on material containing ultrafine mineral.

Bentonite clay has layer and porous structure as pictured on Figure 1, with the distance for each layer about 4.5 ¢ (Rapp, 2009). It also has ability to swell if it is mixed with water, due to the presence of *interlayer* to transfer ions or hydrated molecule with specific size (Arifin, 1997). Those characteristics of bentonite are properly needed for applying as adsorbent in oil decolouring, castor oil, crude palm oil (Labaika, 2006), and in waste treatments especially to adsorb heavy metal and radioactive waste (Wati, 2007; Zamroni, 2002). It also can be applied as catalyst in crude oil hydrocracking process and biodiesel production (Wijaya, 2009).

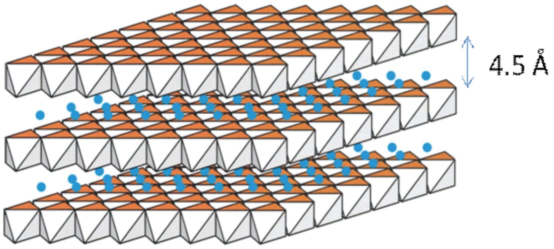

Figure 1. Layer structure of Bentonite (Rapp, 2009)

The restrictiveness of natural bentonite is very narrow distance of interlayer, about 5-10 Å (Darmawan, 2004), so on crude oil hydrocracking processes counters difficult diffusion of the large size heavy fraction of oil residue through bentonite, affects unsmooth by conversion process. There are several techniques in order to enlarge interlayer space of bentonite such as pillarisation (Aziz, 2006). Another developing technique is nano technology that approachs by ultrafine grinding to nanometre scale and follows by leaching (Temuujin, 2001; 2003). The method produces specific characteristic of material, small particle size, enlarging surface area, pores size and volume, so its application as functional material provides better results, such as catalyst, membrane etc.

METHODOLOGY

Raw material used for the research was typical Bogor's bentonite clay. Methods of the research comprised ultrafine grinding and selective leaching. Then, the samples of product of the experiment were characterized by physical and chemical analysis.

a. Ultrafine grinding
   Ultrafine grinding was done in planetary ball mill equipped with alumina balls and steel jar. The amount of the raw material was 50 g with ratio 1:8 of the balls weight. Initial particle size was 200 µm (-325#). The milling was performed in wet condition using methanol 400 ml, with various milling time 10; 30 and 60 hours in 15 Hz velocity.

b. Selective leaching
   5 g of milled sample were leached in 200 ml of sulphuric acid (H_2SO_4) with various concentrations of 3; 5; 7 and 10 N at 80 ºC for 3 hours. Then the leached sample was filtered and washed by 100 ml aquadest and settled in room temperature for 30 minutes. The suspension was then dried off at 80 ºC overnight.

c. Characterization
   Characterization of product was completed by chemical and physical analysis. The chemical analysis of X-Ray Fluorescence (XRF) used Shimadzu XD 7000 for the measurement. While physical analysis were consisted of surface area, pores size, pores volume measurement by BET method using Quadrasorb SI equipped with QuadraWin software, morphological structure was pictured by SEM Jeol JSM 6360LA and particle size was determinated by PSA (particle size analyzer) Delsa Nano C.

RESULTS AND DISCUSSION

Natural bentonite clay of Nanggung, Bogor, West Java, was detected as montmorillonite with rose structure, which associates with silica and it looks porous (Figure 2). The chemical composition of the bentonite is descripted in Table 1. The amount of silica in raw material shows that meso porous silica can be obtained by several process to decrease or even wear off others minerals.

The process began with ultrafine grinding using PBM (planetary ball mill) with various milling time in order to get best milling time with optimum particle size in nano metre scale. The milling process was carried out in wet condition using methanol to obtain effective collision between particles and reduce particle to be attached on jar wall. The result of milling process based on its particle size from PSA is shown in Figure 3.

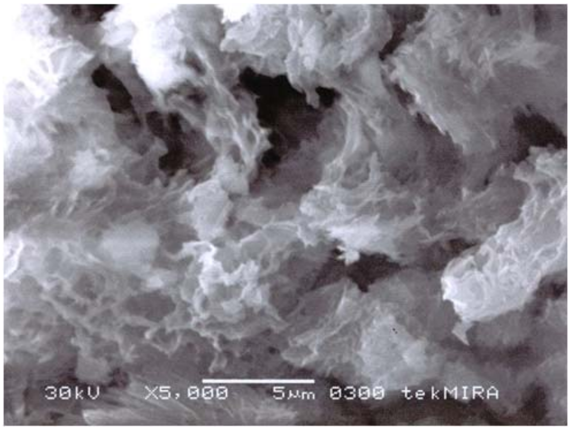

Figure 2. Bentonite structure by SEM

Table 1. Chemical composition of the natural bentonite of Nanggung, West Java

Chemical Composition	Amount (%)
SiO_2	54.13
Al_2O_3	23.09
Fe_2O_3	7.33
MnO	0.19
MgO	0.40
CaO	0.72
Na_2O	0.05
K_2O	0.35
TiO_2	0.48
P_2O_5	0.04
LOI	13.22

Above illustration shows that the 30 hours of milling time performs optimum nano particle sizes (70-80 nm). The longer was the milling time, the particle size obtained was growing back due to agglomeration between particles. The phenomenon occurs because of the collision among particle as the milling time was lifted, produce increasing temperature in jar and influence the sample especially to agglomerate. Therefore, the longer milling time beyond optimum limit will cause over agglomeration that is to enlarge particle size. (Suryanarayana, 2001).

Furthermore, another factor to be concerned is mill rotary speed. The faster is the speed to apply, the higher is the energy applied onto particles. But some certain of milling design equipment can produce limitation of allow maximum speed, which occurs when critical speed reach over the limit, then the balls will attach on jar wall and do not fall down to centre of jar which causes lessen the impact effectively (Suryanarayana, 2001).

After milling process, the sample was continued with leaching using sulphuric acid with various concentration (2N; 5N and 10N). in order to multiply pores amount by excluding metal ions which clogges the pores. The process affects the pore size to be enlarged and is expected to reach meso porous size (2-50 nm). The result of leaching process related to particle size from PSA is shown in Figure 4.

The result shows that the pore sizes enlarge as acid concentration increasing. The phenomenon agree with the theory that the excessive acid

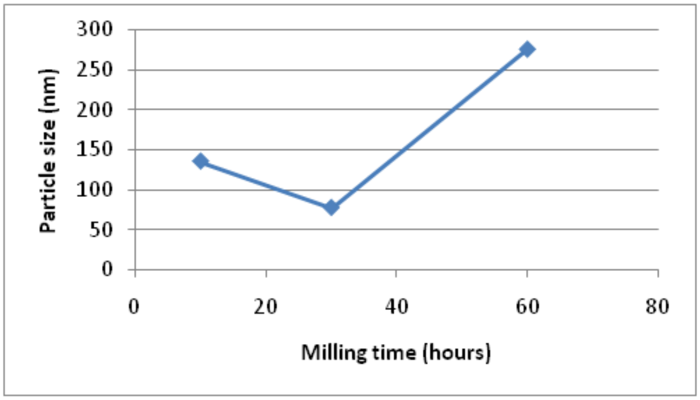

Figure 3. Illustration of milling time related to particle size

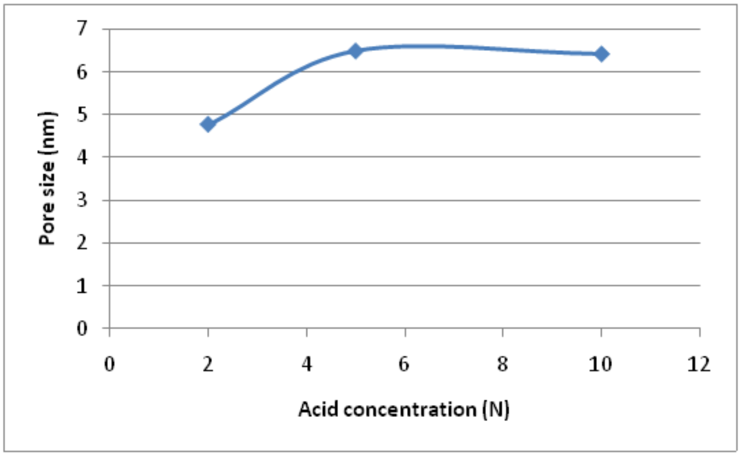

Figure 4. The result of leaching process related to particle size

amounts will dissolve many metal ions and widen the pores. The pore sizes reach 4-7 nm that is considerable as meso porous material (2-50 nm), from initial pore sizes of bentonite 5-10 Å (Darmawan, 2004).

Pore volumes as pore sizes also enlarge as acid concentration increasing which is shown in Figure 5. Pore volume is fully air space in pores, which make the possibility of diffusion to be occurred in catalytic process, adsorption etc. The larger is the air space of material, the better is the adsorbability of it (Rakhmatullah, 2007). Figure 5 pictured that pore volumes generated from the process reach 0.75 mL/g at 10N of acid concentration. It is promising result for catalyst supports, which should have minimum pore volume sizes of 0.5 mL/g.

Specific surface area is influenced by pore sizes and volumes on the material. It will increase as the pore sizes are smaller and the pore volumes are bigger. The higher is the surface area the wider is the contact field between materials, so catalytic and adsorption reaction will get optimum result. The optimum result of specific surface area of bentonite sample reaches 278 m^2/g at 7 N of acid concentration (Figure 6).

The chemical composition of leached bentonite was analysed to know the effect of leaching process that is compared to the natural sample as shown in Table 2. The silica content in the leached product is dominant and other components have already been reduced even worn off compare with natural bentonite (Table 1). So, the porous silica

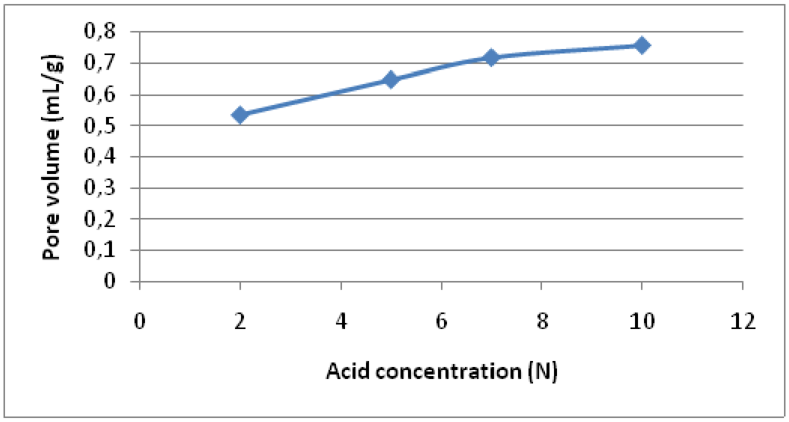

Figure 5. Pore volume results in leaching process

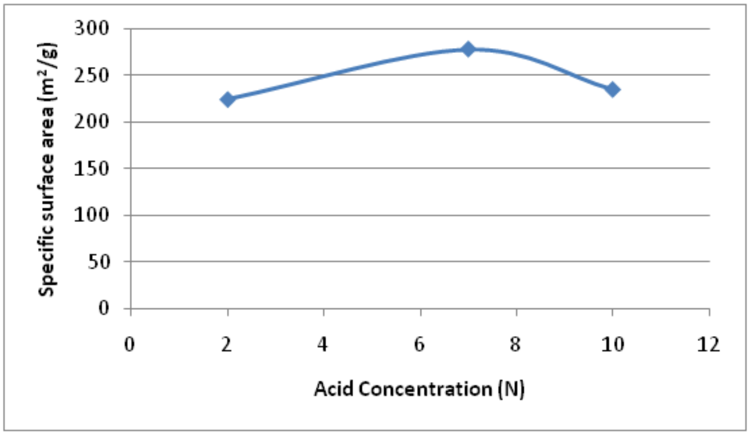

Figure 6. Specific surface area after leaching process

Table 2. Chemical composition of leached bentonite

Chemical composition	Amount (%)
SiO_2	86.21
Al_2O_3	4.96
Fe_2O_3	0.89
MnO	-
MgO	-
CaO	-
Na_2O	-
K_2O	0.20
TiO_2	0.52
P_2O_5	-
LOI	7.13

produced through ultrafine grinding and leaching process have successfully fulfilled the requirement characteristic of meso porous nanomaterial, which has particle size in the range of 0-100 nm and 2-50 nm of pore sizes.

Nowadays nano material is very developing and demanding for industries. The product is promising material to be utilized in several industries such as follows:

a) Catalyst support

Generally, the specifications of the required catalyst support are high specific surface area, large pore sizes and volumes, very small amount or even undetected of impurities which can destruct the catalytic reaction. The result of nano particle bentonite in this research is very potential to be used as catalyst support. Some forms of catalyst support are shown in Figure 7.

Otherwise, porous material can be used as substrate on catalytic converter (Figure 8) which is installed at vehicle exhaust gas equipment. The function of the material is to convert hazardous emission substances that is

Figure 7. Catalyst support material

produced by fuel combustion process, such as HC, CO, NOx, to H_2O, CO_2 and N_2 (Rees, 2009). The small particle size and high surface area will enhance catalytic converter performance.

b) Metal adsorbent

Nano particles bentonite also can be applied as substrate on magnetic adsorbent which is used for adsorbing heavy metals from laboratorium waste or industrial waste. Nano bentonite and magnetic particle are mixed in certain ratio (Figure 9) then it moulds and installs in waste water disposal pipe to adsorb heavy metal (Figure 10). This material is renewable and it can be reused (Vogt, 2009).

c) Smart textile

Smart textile is fabric textile implied with nano bentonite particle. This material is greasy and able to absorb water so it will make non rumpled cloth and able to absorb sweat properly (anti bacteria) as natural deodorant. Researchers in China developed this invention and designed it in mass production (Hinestroza, 2009). Figure 11 shows fibre textile implied by nano bentonite particle.

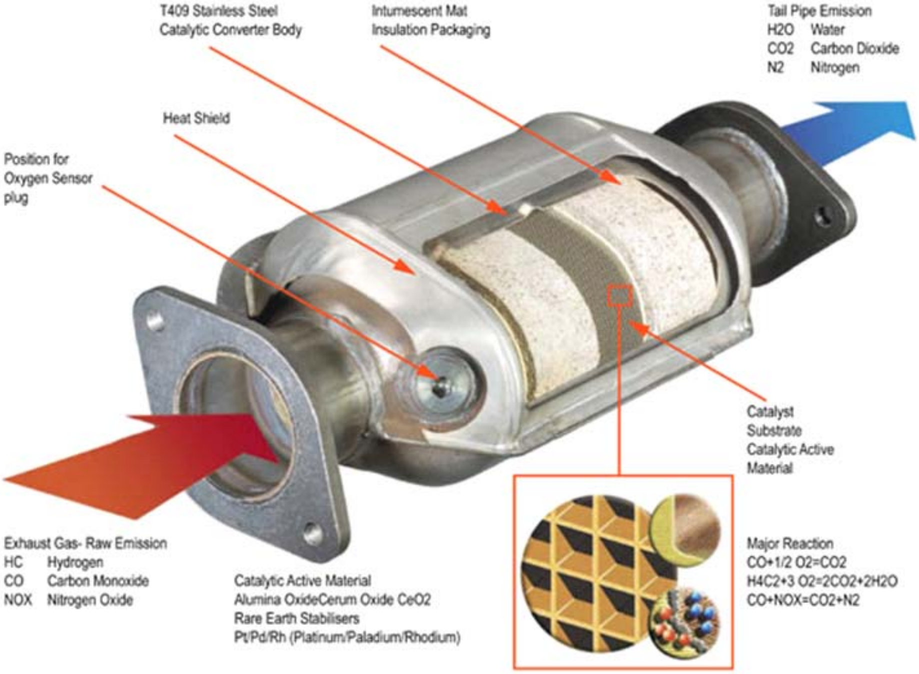

Figure 8. Porous material as substrate on catalytic converter (Rees, 2009)

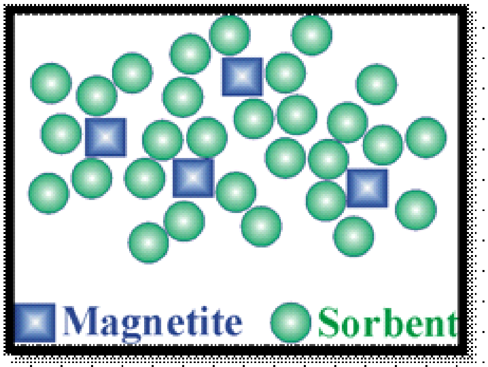

Figure 9. Magnetic particle scheme imply in bentonite substrate

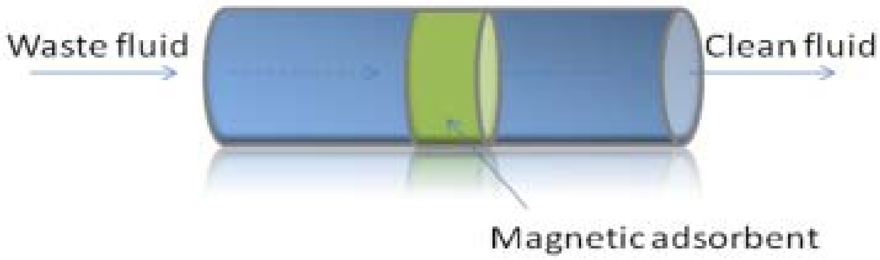

Figure 10. Magnetic adsorbent installation scheme in waste disposal pipe

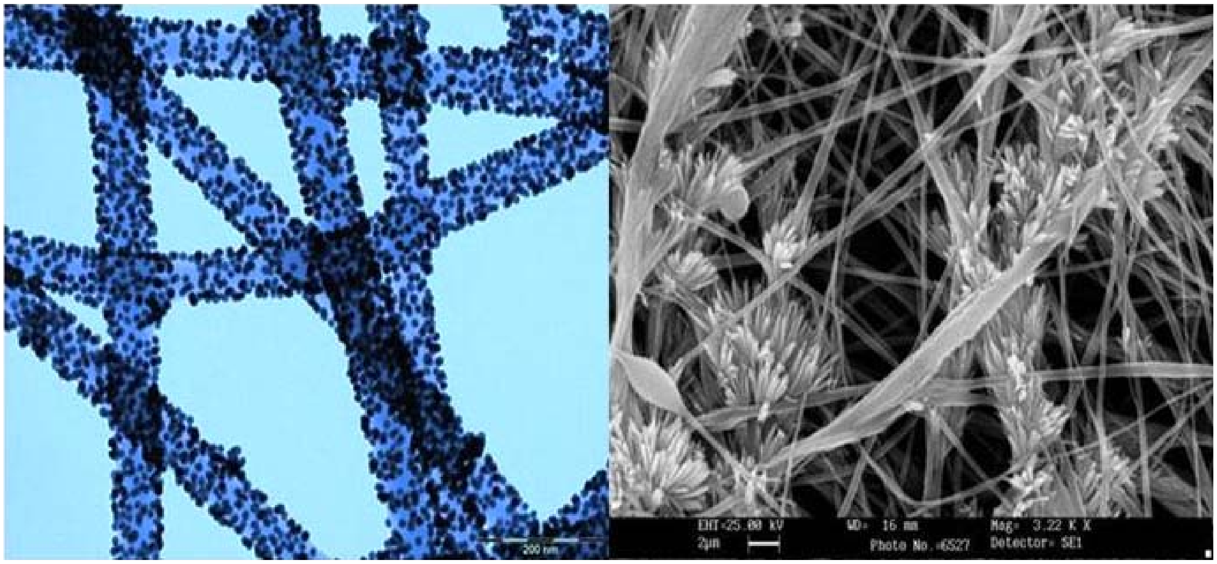

Figure 11. Fibre textile implied with nano-gold particle (Hinestroza, 2009)

CONCLUSION

– Porous silica has been succeeded to be synthesised from bentonite by ultrafine grinding and leaching.

– Ultrafine grinding with methanol as the solvent (wet milling) within 30 hours, produces bentonite in 77.4 nm of particle size.

– Leaching process using sulphuric acid can increase SiO_2 content of 54.13% up to 86.21% and to decrease Al_2O_3 and Fe_2O_3 respectively from 23.09% and 7.33% down to 4.96%, and 0.89%.

– The leaching process generates porous silica material which has 278 m^2/g of surface area; 0.75 mL/g of pores volume and 6.5 nm of pores size (meso pore).

– The meso porous silica with properties mentioned above is promising to be utilized as catalyst support, metal adsorbent and smart textile.

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