FINE GRINDING OF HEMATITE IN PLANETARY MILL AND ITS APPLICATION AS DYE DECOLORIZATION CATALYST

ROSHAIDA BINTI ARBAIN

UNIVERSITI SAINS MALAYSIA

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by

ROSHAIDA BINTI ARBAIN

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

d_{50}	mean particle size/ diameter
d_{av}	equivalent spherical particle diameter
E	impact energy of grinding medium
m	mass of grinding media
v	relative velocity of the grinding medium
ω	mill rotational speed
t	time
E_m	specific energy consumption
Ws	the weight of the test sample
P(t)	power consumed in grinding for a given grinding time
R^2	coefficient of determination
σ	density
S	specific surface area
2θ	peak positions
D_v	crystallite size
ε	lattice strain
β	integral breadths profile
A_0	areas of feed under the peak
A_t	areas of ground particles under the peak
a / c	unit cells parameters of ground samples
a^0 / c^0	are the unit cell parameters for untreated samples
λ	wavelength
C_o	initial concentration of dye

C_t	concentration of dye at reaction time
H_2O_2	hydrogen peroxide
$^{\bullet}OH$	hydroxyl radical
$HO_2^{\bullet}$	hydroperoxyl radicals
OH^-	hydroxide ion
H^+	hydrogen cation
CO_2	carbon dioxide
H_2O	water
Fe(III)	ferric ion ($Fe^{3+)}$
Fe(III)	ferrous ion (Fe^{2+})
O_3	ozone
α-Fe_2O_3	hematite
γ-Fe_2O_3	maghemite
Fe_3O_4	magnetite
FA	fly ash
SiC	silicon carbide
ZrO_2	zirconium oxide
CeO_2	cerium oxide
WC-Co	tungsten carbide-cobalt
CaO/TiO_3	calcium titanate
SiO_2	silicon dioxide/ silica
MnO	manganese oxide
Cr_2O_3	chromium oxide
CuO	copper oxide
SO_3	sulphur trioxide

KBr	potassium bromide
H_2SO_4	sulfuric acid
NaOH	sodium hydroxide
P	pump
HO	untreated hematite particles
HB	ground hematite particles at 400 rpm, 10 h
HC	ground hematite particles at 600 rpm, 10 h
i.e	that is

LIST OF ABBREVIATIONS

XRF	X-ray Fluorescence
BET	Brunauer-Emmett-Teller
SSA	Specific Surface Area
XRD	X-ray Diffraction
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
UV	Ultra Violet
AAS	Atomic absorption spectrometry
RR3B	Remazol Red3B
AOPs	Advanced Oxidation Processes
DOC	Degree of Crystallinity
ICDD	International Center for Diffraction Data
FWHM	Full-Width at Half Maximum
BPR	Ball to Powder Ratio

PENGISARAN HALUS HEMATIT DALAM PENGISAR PLANET DAN APLIKASINYA SEBAGAI PEMANGKIN UNTUK PENYAHWARNAAN PEWARNA

ABSTRAK

Pengisaran halus hematit dalam pengisar planet telah dilakukan dengan mengubah halaju putaran pengisar dan masa pengisaran dalam keadaan kering dan basah. Produk terkisar dicirikan berdasarkan luas permukaan spesifik, kesan mekanokimia menggunakan Belauan Sinar-X dan Spektroskopi Infamerah dan morfologinya. Luas permukaan bernilai 40.2 m^2/g diperoleh melalui pengisaran dalam keadaan kering dan basah dengan penggunaan tenaga masing-masing adalah 76.8 kWjam/kg dan 30.7 kWjam/kg. Produk terkisar hematit pada 600 *rpm* selama 10 jam dan 400 *rpm* selama 25 jam dalam keadaan basah mengalami perubahan fasa sepenuhnya daripada hematit kepada magnetit manakala tiada perubahan fasa berlaku bagi produk terkisar hematit dalam keadaan kering. Darjah penghabluran bagi pengisaran dalam keadaan kering dan basah masing-masing berada dalam julat 5.76% hingga 49.81% dan 4.39% hingga 56.1% dengan produk terkisar mengalami pengembangan atau pengecutan kekisi kristal. Saiz kristal minimum diperoleh dalam pengisaran kering pada 600 *rpm* selama 10 jam adalah 17.1 nm dan terikan kekisi 0.846. Kesan mekanokimia disokong oleh perubahan yang berlaku pada jalur Infra merah. Produk terkisar dalam keadaan kering dan basah mengalami beberapa peringkat pengagregatan. Pada peringkat akhir eksperimen, produk terkisar terpilih digunakan sebagai pemangkin untuk penyahwarnaan pewarna reaktif merah3B (RR3B) secara berkelompok. Penyahwarnaan pada kadar 95.8% dalam masa 10 min dicapai bagi partikel bersaiz halus iaitu 75 nm dengan kadar pelarutan ion Fe yang minimum, iaitu kurang daripada 5 mgL^{-1} yang mematuhi Peraturan-Peraturan Kualiti Alam Sekeliling (Efluen Perindustrian) 2009. Proses penyahwarnaan pewarna RR3B secara berterusan juga dilakukan dan didapati penyahwarnaan sepenuhnya diperoleh dengan pelarutan ion Fe yang rendah yang menunjukkan bahawa produk hematit terkisar boleh digunakan sebagai pemangkin dalam applikasi rawatan air sisa bagi industri tektil berskala besar.

FINE GRINDING OF HEMATITE IN PLANETARY MILL AND ITS APPLICATION AS DYE DECOLORIZATION CATALYST

ABSTRACT

Fine grinding of hematite in planetary mill was carried out by varying the mill rotational speed and grinding time in both, dry and wet conditions. The ground samples were characterized in terms of the specific surface area, mechanochemical effect through X-ray diffraction and Infrared Spectroscopy and its morphology. Specific surface area of 40.2 m^2/g was achieved through dry and wet grinding condition with energy consumed of 76.8 kWh/kg and 30.7 kWh/kg respectively. Ground hematite in wet condition at 600 rpm for 10 h and 400 rpm for 25 h exhibits complete phase transformation from hematite (α-Fe_2O_3) to magnetite (Fe_3O_4) whilst in dry condition, no phase changes was observed. The degree of crystallinity ranges from 5.76% to 49.81% and 4.39% to 56.1% in dry and wet conditions, respectively with variation in lattice parameters either expansion or shrinkage. The minimum crystallite size obtained was 17.1 nm which exhibits lattice strain of 0.846 in dry grinding condition at 600 rpm for 10 h. The mechanochemical effect is supported by changes of IR bands. The ground particle exhibits some level of aggregation in both grinding conditions. Finally, the selected ground samples were used as catalyst for decolourization of reactive dye, Remazol Red3B (RR3B) in batch mode. The smaller particle size of 75 nm decolourized at the rate of 95.8% within 10 min with minimum iron leached (<5 mgL^{-1}) which fulfill the Environmental Quality (Industrial Effluent) Regulations 2009. The continuous mode for decolorization of RR3B was carried out and complete decolorization was achieved with low iron dissolution which demonstrates the possibilities of using ground hematite as catalyst for large-scale textile industry wastewater treatment applications.

CHAPTER ONE

1.0 Introduction

The important of fine grinding has increase with the demand for fine particles in various manufacturing industries such as paper, paint, plastic, pharmaceuticals, ceramics, cosmetics, foods and fine chemicals. These industries need fine particles with stringent specifications in terms of particle size, particle size distribution and particle shape as well as chemical composition (Palaniandy, *et al*., 2008).

Generally, ultra-fine grinding is known as energy-intensive process in the overall process in comminution, which to provide materials in proper fine size ranges for the required properties of the final product, especially for producing particles in micron sizes (Jankovic, 2003). It is an intermediate case between coarse grinding and mechanical activation. In the same way to coarse grinding, fine grinding is intended for size diminishing, but the huge amount of energy which was delivered by the mill led to microstructural changes in the particles which terms as mechanochemical effect, while mechanical activation is worked to change the structure by the reactivity determination (Palaniandy and Jamil, 2009).

Recently, fine grinding has the potential to develop the mineral processing industry due to the benefits attained through being able to economically produce nanoparticles (Wang and Jiang, 2007). Figure 1.1 illustrates an approach to synthesize nanoparticles i.e either to break or dissociate solids into finer pieces or assemble atoms together. Most of nanoparticles are generated by using crystallization, direct generation or other similar techniques, which is often referred to as “bottom up” or build up process. In the other method that will discuss further in this study, referred to as “top down” or break down process, i.e. larger particles are reduced through mechanical grinding to achieve the desired nanoscale particles (Balaz, 2008).

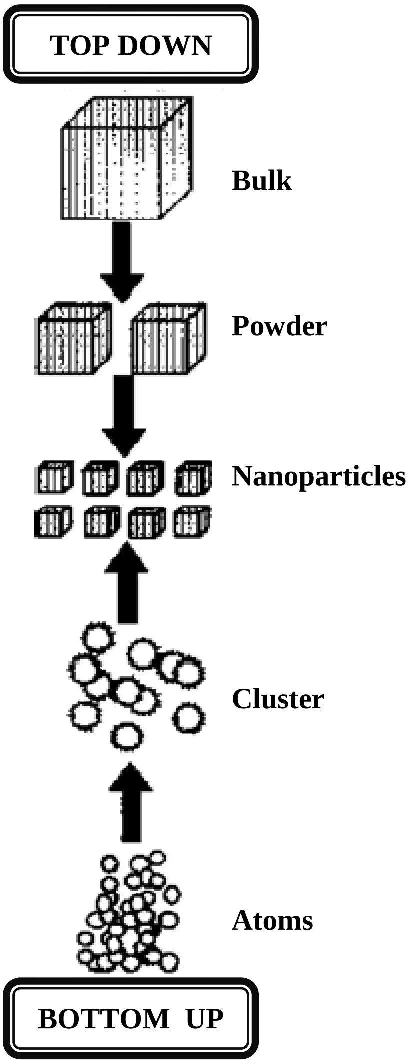


Figure 1.1: The top down and the bottom up techniques for synthesis of nanoparticles (Balaz, 2008)

As particles become smaller, their properties can change in mysterious and useful ways. This change in properties is often due to their highly stressed surface atoms which are very reactive. Recently, iron oxide nanoparticles have been used as a functional environmental material (Khedr, *et al.,* 2009; Xu, *et al.,* 2008; Wang, *et al.,* 2009; Bakardjieva, *et al.,* 2007). It has also been found to reduce effectively the generation of dioxin, a substance that has lately become the subject of serious environmental concern (Toda Kogyo Corp, n.d). It is well known that the shape and size of catalysts play crucial roles on their catalytic performances.

Furthermore, aside from size reduction, mechanical grinding can induce phase transformations of α-Fe_2O_3 to (γ-Fe_2O_3, Fe_3O_4) or vice versa depending on the environment of grinding performed (Zdujic, *et al.*, 1998; Sanshez, *et al*., 2007). Grinding mills typically used in fine grinding includes the shaker, planetary, jet, oscillating, vibration and attritor mills, all of which are classified as high-energy mills. In fact, the selection of the appropriate grinding parameters for specific equipment to produce fine powders especially nanoparticles is necessary which involves preliminary experimental work.

2.0 Application of hematite as catalyst for dye removal

Generally, nano-sized materials exhibit novel physical and chemical properties and consequently, fine grinding of hematite particles will intentionally studied. In fact, iron oxides are recently used as catalyst due to easy handling which their availability in powder form, relatively low cost, non-toxicity and environmentally friendly characteristics (Khedr, *et al.,* 2009; Xu, *et al*., 2008; Wang, *et al*., 2009; Bakardjieva, *et al*., 2007). The catalysts are currently utilized on large scale in a laboratory, industrial and environmental processes. The high catalytic efficiency in heterogeneous catalysis can be achieved by the use of smaller particle sizes which provided higher surface area to further enhance the rate of reaction (Xu, *et al*., 2008).

On the other hand, synthetic dyes are extensively used to color many different products such as textiles, paper printing, colour photography and cosmetics. Although dye makes our world beautiful, they bring pollution. It is estimated that 10-15% (10-200 mgL^{-1}) of the total dye used for colouring is lost in the effluent during dyeing process (Pirillo *et al*., 2008). A variety of physical, chemical and biological methods are used for treatment wastewater from chemical dye production industry although most of them were found to be not effective and expensive (Khedr, *et al.*, 2009).

An alternative method for removing dye from wastewater is advanced oxidation process by using hematite particles where the local resources can be exploited to produce Fe_2O_3 nanopowder. The aim of this work is to value add locally available hematite through fine grinding in planetary mill to be use as catalyst for textile dye removal in wastewater.

1.2 Problem Statement

The direct synthesis of iron oxide nanoparticles by chemical synthesis such as gas phase, liquid phase, two phase, sol-gel, high pressure and hydrothermal methods are commonly used in industry although it is found to be very complicated and expensive. Mechanical grinding is a very convenient technique and promising way to produce nano-particles powder (Wang and Jiang, 2007).

In particular, during the initial stages of grinding a mixed powder, a reduction of the grain size occurs down to the limit of fragmentation, while the huge amount of energy delivered by further grinding can produce a phase transformation, mechanochemical effect, or the recovery of the grains. Therefore, the ground particles may experience structural defects, leading to reduction in the degree of crystallinity of particles. The mechanochemical effect can be quantified through the degree of crystallinity, crystallite size, lattice strain, and lattice parameters (Palaniandy and Jamil, 2009). Thus, the study on the control of the operational parameters and grinding environments is very essential to optimize the size reduction process and mechanochemical effect of the ground particles.

As colors are the most notorious characteristics of dye wastewater and have a strong negative impact on aquatic environment, it is important to remove these pollutants from wastewater. The present of dye in wastewater will reduces sunlight penetration in water system which causing negative effect on photosynthesis. Thus, aquatic ecosystem can be seriously affected (Koprivanac and Kusic, 2007). From an environmental point of view, the hematite which produces through mechanical grinding has the possibility to decolorize dye.

On the other side, Malaysia’s iron ore reserves are estimated about 82.2 million tonnes where the mines located in Pahang, Johore, Perak and Terengganu (Malaysian Chamber of Mines, 2009). Hence, for protecting the environment and to meet the stringent government law, this research proposed as an effective and economical way of dye-containing wastewater treatment by using Fe_2O_3 as catalyst which locally available in Malaysia.

1.3 Research Objective

The main objective of this study is to produce hematite nanoparticles through fine grinding in planetary ball mill and to use ground hematite for decolorization of dye.

The measurable objectives are;

1. To determine the influence of mill rotational speed and grinding time on the product fineness, particle morphology and mechanochemical effect through changes in phases, degree of crystallinity, crystallite size and lattice strain during dry and wet grinding conditions in planetary mill.
2. To evaluate the performance of hematite particles as catalyst through the decolorization efficiency and iron leaching in batch and continuous process.

1.4 Scope of Study

The scope of this study includes fine grinding of hematite in planetary mill by varying the mill rotational speed and grinding time in dry and wet conditions. The mill rotational speed chosen were 200, 400 and 600 rpm, whilst the grinding times were 1, 5, 10, 15 and 25 h. The factors affecting the fine grinding in planetary mill were identified in terms of physical and chemical characteristics through chemical composition (XRF), mineral phases (XRD), BET surface area analysis, particle size analysis (PSA), morphological analysis (SEM), Transmission Electron Microscopy (TEM) and chemical bonding (FTIR). The selected hematite particles produced from mechanical grinding were tested as catalyst to decolorize synthetic dye Remazol Red3B (RR3B) in a batch system. The influence of reaction parameter such as effect of pH values, amount of catalyst loading, concentration of H_2O_2 and temperature were examined in batch mode series, as well. The best catalytic conditions for hematite particles were determined to get a good performance in decolorization of dye in batch system by observing the percentage of color removal from its characteristics absorption using UV-Vis spectrophotometer and iron dissolution using Atomic Absorption Spectrophotometer (AAS). In addition, an attempted of performing continuous process for decolorization of RR3B under the best reaction conditions obtained from batch experiment were studied, as well. The synthetic dyes were collected from the batik industry in Penang, Malaysia.

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

Grinding is an oldest engineering process as it was used since the Stone Age. Traditionally, the mills have been operated by human muscles and the energy input was created by rubbing, rolling and knocking with pestles and grinding stones. This basic grinding mechanism is still used in the modern grinding mills, especially for media and roller mills. As the demand for fine particle is emerging, due to its advantage of larger specific surface area and high activity of the particle surface there is need to grind the particles finer and currently the demand is focusing at sub-micron and nanometer (Stein, 2005; Yokoyama and Inoue, 2007).

Mechanical grinding is one of the common methods used to prepare ultrafine particle even in nano-meter range. However, grinding at this particle size range is exorbitant due to low mill throughput with high energy consumption. Therefore, it is essential to improve the operating and design parameter with optimum feed in order for substantial beneficial in terms of energy consumption and cost. To accomplish this, appropriate mill selection and operation at optimum grinding conditions are necessary (Cho, *et al*., 2006).

The main aim of grinding is for size reduction and this phenomenon is true for the case of coarse grinding (De Castro and Mitchell, 2002). On the other side, if the grinding is performed in high energy mill, the resulting particulate powders will experience relaxation from brittle fracture to ductile fracture along with rise in strain. As a result, the dislocation flows take place in the particles. Consequently, it leads to the growth of structure distortion. Those structural changes determine the reactivity of the particles (Pourghahramani and Forssberg, 2006a).

Among the high energy mills are vibratory mill, planetary ball mill, jet mill and stirred mill. This mill varies in terms of capacities, efficiencies of grinding and additional arrangements such as cooling, special systems for measuring the temperature and/or pressure. Apart from that, they have certain features in common, where the grinding ability of these devises is controlled by the frequency of impacts and the modes of stress that influence the nature of structural changes besides particle size reduction (Wieczorek-Ciurowa and Gamrat, 2007). The variety of mechanical grinding devices is attributable to the diversity in the requirements for the grinding and the properties of the materials to be ground.

2.1 High-energy grinding

High energy grinding is one of the method produce submicron and nanoparticles. As mention earlier, grinding mills typically used in the production of ultrafine particles are planetary ball mill, jet mill, oscillating mill, vibration mill and stirred mill, all of which are classified as high-energy mills. The advantages of preparing ultrafine by high energy mill are its more economical, simple operation and high yield than chemical synthesis (Wang and Jiang, 2007). Furthermore, latest development in high energy mill has the capability to produce ultrafine particles compared to conventional ball mill due to the impose energy by the mills to the particles which are typically 100-1000 times higher than the conventional mills (Balaz, 2008). Generally, the product form the high energy mills are mechanically activated and the particles possess a number of new useful characteristics such as higher reactivity, lower sintering temperature, higher density and improved mechanical and electrical properties (Fokina, *et al*., 2004). This phenomenon very much depends on the type of stress impart by the mill on the particles.

The stress of particles in media type mills are affected by impact, pressure and shear forces between grinding media each other and between the mills parts (Stein, 2005). These stresses allow a dramatic change of structure and surface properties of solids to be induced besides particle size reduction (Pourghahramani and Forssberg, 2006a). Figure 2.1 shows different type of stress of particle which took place in the media type mills.

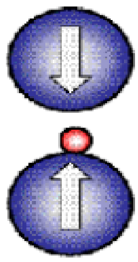
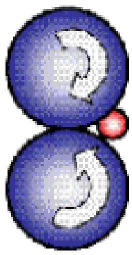
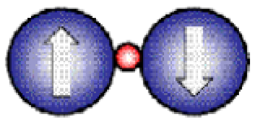
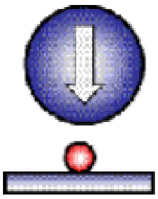
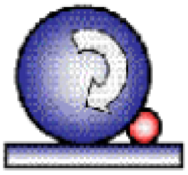
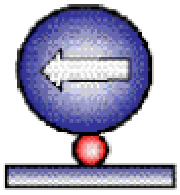
Falling balls	**Stress of particle in media mills**		
	Impact (collision and stroke)	**Compression**	**Shear force**
Ball-powder-ball			
Ball-powder-wall			

Figure 2.1: Different type of stress of particle in media mills (Stein, 2005)

Tumbling ball mills can be operated at different speed levels, which will influence on type of stress imposed such as impact and shear. Vibration mill with their high frequency motion are dominated by impact grinding, whereas centrifugal mills tend more to shear and pressure stressing. Similar to tumbling ball mills, the planetary ball mills create different media motion depending on the rotation of mill pots and revolving base disk (Stein, 2005).

The high energy mill also leads to contamination and formation of agglomerates during grinding which are the main disadvantages especially those particles which was ground in media based mill. The main contributor of impurities during high energy mill in media type mills are iron from the grinding media and mill lining. In order to avoid iron or other contamination of grinding media made from tungsten carbide or ceramics is desirable, when possible to have the grinding vessel and the grinding medium made of the same materials as the particles being ground. According to Balaz (2008), the contamination can also be reduced by using surfactants and grinding at shortest time.

Furthermore, the ground particles exhibit higher surface energy which leads to the agglomeration phenomenon in order to reduce the surface energy (Balaz, 2008). There are three stages of interaction between particles, which are adherence, aggregation, and agglomeration. In the adherence stage, ground particles will coat the grinding bodies. Adherence interferes with the grinding process, and further adhesion may also take place during storage and transport. At the aggregation stage, particles affect the grinding process through the product’s quality. Agglomeration is defined as a very compact, irreversible interaction of particles in which chemical bonding may also play a role. Agglomeration is detrimental to the grinding and the quality of the product (Jamil and Palaniandy, 2009). Currently, grinding aids are used to prevent particle agglomeration during the production of fine particles (Choi, *et al*., 2010).

Besides media type mills, jet mill which is considered as semi autogeneous or autogeneous is widely use for ultra fine grinding process for particle size below 10 µm. Jet mills possesses several advantages include the ability to produce micron-size particles with narrow size distribution, the absence of contamination, and the ability to grind heat sensitive materials. Although it consumes high energy, the particle to particle impact breakage mechanism which leads to minimal contamination, sets jet mill as a promising device for producing ultrafine particles (Palaniandy *et al*., 2008). Among all the high energy mills, the planetary ball mill has the capability to produce ultrafine particles in nanometer range with mechanochemical effect and phase transformation as reported by several authors for iron oxide and other minerals (Chen, *et al*., 2007; Sanshez *et al*., 2004, 2007).

2.2 Planetary ball mill

Planetary ball mill is widely used for ultra-fine grinding and synthesis of advanced materials and currently there are planetary ball mill which are operating in continuous mode, as well. Besides particle size reduction, this mill is being used for mechanical alloying and mechanochemical-synthesis operations. In conventional ball mills, the gravity field becomes the main limiting factor as the impact energy is too low. The planetary mill overcomes this limitation by supplying a strong acceleration field that produced maximum collision with higher impact energy (Chaira *et al*.

2007). Furthermore, this mill exhibits advantages such as low material loss, the cost of the equipment is significantly lower than other types of mill such as jet mill, excellent homogenization and particles with high superficial area are easily generated in a very short time. Similar characteristics can be observed in stirred mill (Dos Santos and Costa, 2006).

Although planetary mill exhibits massive particle size reduction, contamination due to grinding media is still an issue. Figure 2.2 shows the amount of contamination that cooperated in SiC powder by grinding in planetary ball mill with grinding media of ZrO_2+CeO_2 and isopropyl alcohol as the dispersant. Longer grinding period increase the contamination in the ground products due to strong friction between the grinding media, the powder, the coating and a very small regions of the jar wall not coated, which introduced small fragments originating from each of those places (Dos Santos and Costa, 2006).

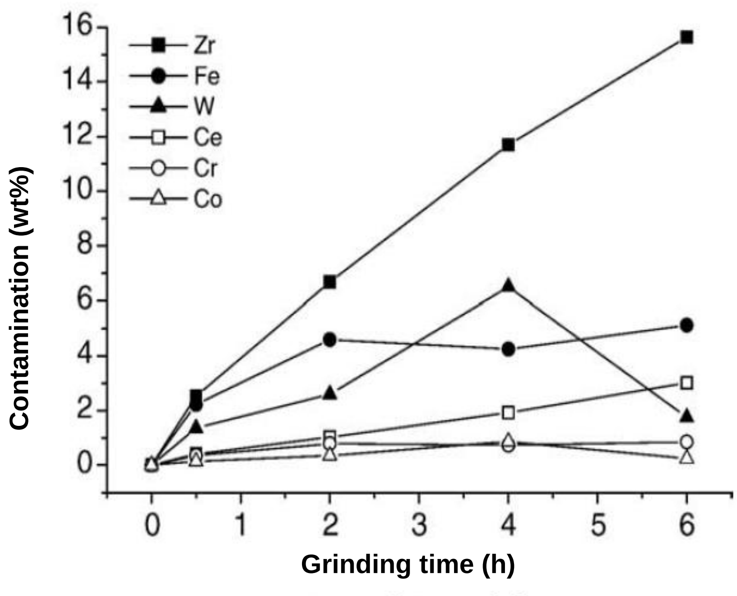


Figure 2.2: The amount of element introduced during grinding of SiC powder in planetary ball mill at different grinding times (Dos Santos and Costa, 2006)

Another aspect that has to be considered during grinding in planetary ball mill is agglomeration. Pourghahramani and Forssberg (2007) have studied the effects of mechanical activation on the reduction behavior of hematite concentrate in planetary ball mill and vibratory mill. Figure 2.3 shows the results obtained for mean particle size (d_{50}) of ground products with different value of grinding media surfaces at various grinding period which results typical agglomerate of hematite. The agglomeration was indicated by increased in d_{50} values after prolonged grinding with higher surface area media as supported by image from SEM analysis. Moreover, the increased of temperature by prolonged grinding in planetary mill had created a problem in the system, as well. Therefore, the use of a copper disk as a simple heat sink for planetary mills had been proposed by Kleiv (2009) in order to limit or slow down the temperature increase during prolonged grinding.

2.2.1 Grinding mechanism in planetary ball mill

Planetary ball mill consists of a revolving base disk and rotating mill pots partially filled with material to be ground and grinding balls. Figure 2.4 presents the schematic configuration of the planetary ball mill. Materials are ground by the large centrifugal force generate when both base disk and pot rotated simultaneously and separately at high speed in opposite direction. Such high-speed rotation results the balls to move strongly and violently, leading to large impact energy of balls that improves grinding performance (Chaira *et al*., 2007).

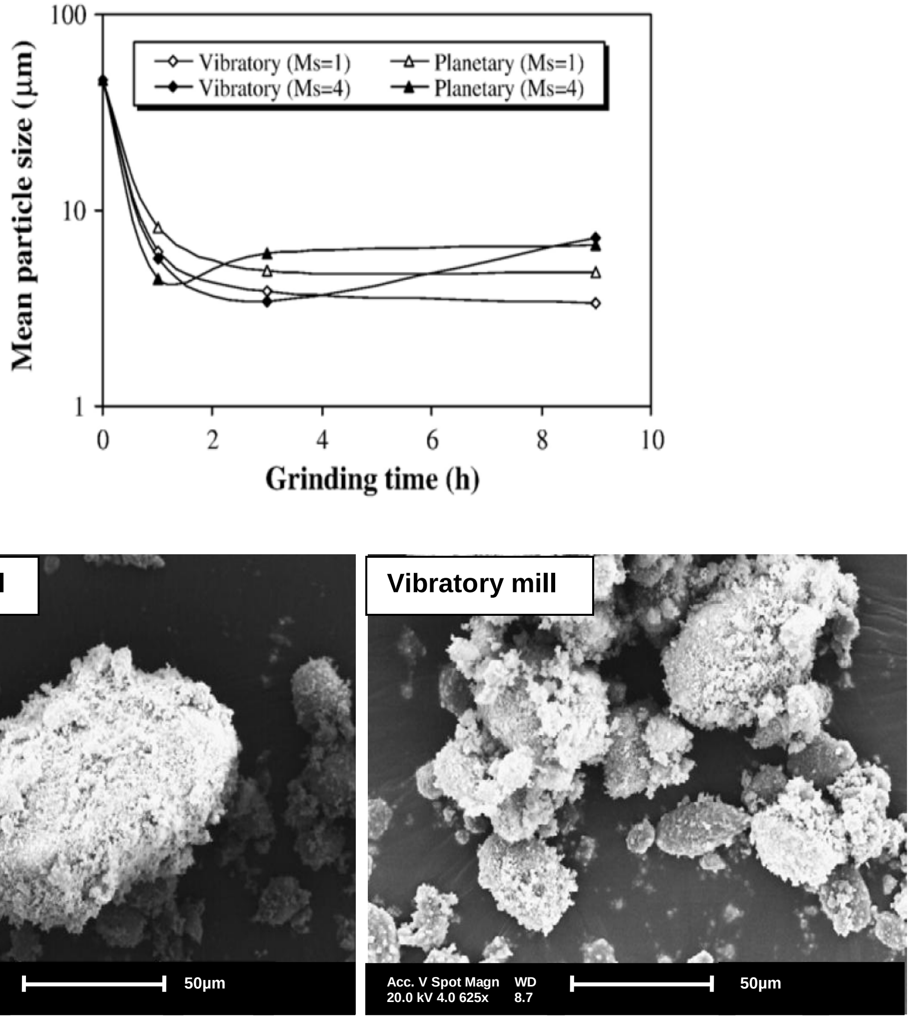


Figure 2.3: Values of d_{50} for initial and ground hematite obtained with different media surfaces at various grinding times and their morphologies after 9 h grinding (Pourghahramani and Forssberg, 2007)

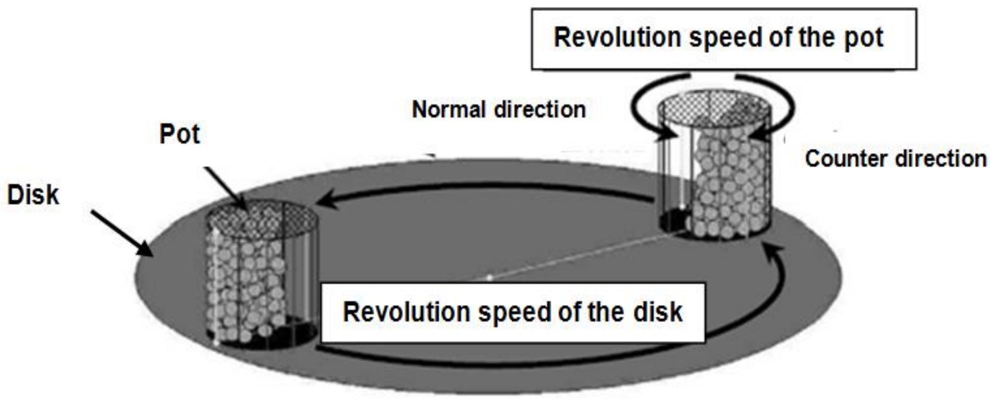
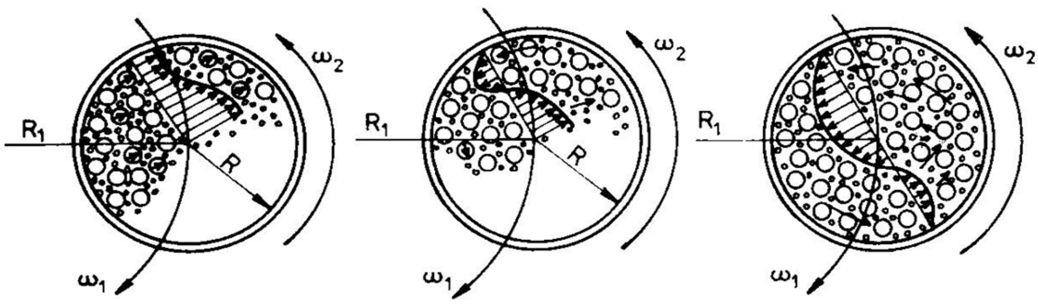


Figure 2.4: Schematic configuration of the planetary ball mill (Mio *et al.*, 2004)

As planetary mill use balls as grinding media, the movement of the balls can be describe in three different motions; (a) cascading, (b) falling or cataracting, or (c) hurricane as illustrate in Figure 2.5. In cascading motion, the feed moves counter to the rotation of the pot. Velocity gradients in the ball-powder-ball, as well as between ball-powder-wall, create favorable conditions for effective attrition (Figure 2.5a). In the catarating mode of operation, the feed is concentrated in the narrow zone, where it tumbles along a curved trajectory (Figure 2.5b). A similar trajectory has been detected in the so-called hurricane mode of operation, although in this case the material is distributed over the entire volume of the drum (Figure 2.5c). The hurricane mode of operation is characterized by the combined action of compression, shear and impact stresses. Shear resulting from the attrition of particles caught between beads is the prevailing mode of stress in attritors. The action of shear forces is supplemented with compression between the ball-powder-ball and ball-powder-wall (Tkacova, 1989). Specifically, the impact stress force plays a role in the rapture of particles while the shear and compression play an important role in the formation of structural defects (Gonzalez *et al*., 2000).



(a) **(b)** **(c)**

Figure 2.5: Type of ball motion in planetary ball mill (Tkacova, 1989)

2.2.2 Parameters affecting ultrafine grinding in planetary mill

In order to improve the processes in a planetary mill, much attention should be given on optimizing the grinding parameter to control the particle size reduction, mechanochemical effect and particle morphology. The main parameters effects on grinding that will be discussed further in this study are nature of grinding mode, grinding speed and grinding time. The other essential parameters are amount of material filling, feed size, charge ratio and material of media grinding (Suryanarayana, 2004).

2.2.3 Nature of grinding mode

Two grinding modes, dry and wet contidions are commonly applied in the grinding process to observe the effects on the structural changes on the ground products. Dry grinding process was carried out in air or argon atmosphere whilst in the wet grinding process different appropriate liquids/ surfactant such as distilled water, ethanol or acetone had been used depending upon material of interest (Sorescu and Diamondescu, 2010; Zhang *et al.*, 2008; Sanchez *et al.*, 2007; Goya, 2004). For comparison, wet grinding causes shearing along the cleavage planes whereas dry grinding fractures the crystal. Furthermore, wet grinding proceeds with the preferential formation of new surfaces while little bulk deformation takes place in particles (Charkhi *et al.*, 2010). There are two mechanisms for the effect of the surfactant while performing the grinding in wet condition;

- The surfactant absorbed on the surface of the brittle materials can reduce the hardness of the materials.
- The surfactant can reduce the viscosity of the slurry of powder mixture (Zhang *et al.*, 2008).

The grinding rate decreased with increase of either viscosity or surface tension of the grinding medium. Zhang *et al*. (2008), has reported the effect of different type of grinding medium as shown in Table 2.1, on the nanostructure of tungsten carbide/cobalt (WC-Co) composite powder in planetary ball mill. The best level for WC grain size reduction is by using ethanol, but the best level for particle size reduction is by using distilled water. The reason is, ethanol with lower surface tension may be absorbed on the surface of WC and its micro-crack, and also reduce the hardness of WC. Distilled water has higher surface tension and lower viscosity, thus the reduced viscosity of the slurry may help to reduce the particle size.

Table 2.1: Surface tension and viscosity of the grinding medium in air at 20° (10^{-3} Nm^{-1}) (Zhang *et al*., 2008)

Grinding mediums	**Surface tension (10^{-3} Nm^{-1})**	**Viscosity (cP)**
Distilled water	72.75	1.002
Ethanol	22.8	1.200
Acetone	23.7	0.3
75% Ethanol water solution	25.28	-

Sanchez *et al*. (2007) studied the conditions for production of hematite nanoparticles in air and ethanol. The results show that by grinding in ethanol, hematite nanoparticle was obtained without any change whilst a new maghemite phases (γ-Fe_2O_3) were observed by grinding in air. This transformation is due to the greater energy transferred to the powder for the mill, contrary to the grinding in ethanol where this avoids the direct contact between powder and elements of the mill.

2.2.4 Grinding speed

Grinding speed is an important operational parameter in the grinding process. The faster the mill rotates, the higher will be the energy input imparted onto the materials which directly relates to the transfer of impact energy from the grinding media to the materials being milled. The impact energy of balls, *E* is given in Equation 2.1.

$$E = 1/2\ mv^2 \qquad \text{Equation 2.1}$$

where, m = mass and v = is the relative velocity of the grinding media (Suryanarayana, 2004).

Besides that, at higher grinding speeds the temperature of the grinding chamber may reach a high value, thus more energy is transferred to the powder particles resulting in faster development of a surface area and promotes mechanochemical effect. However, contrary results were obtained during mechanochemical synthesis of $CaTiO_3$ in planetary ball mill. Figure 2.6 shows the particles became coarser as the mill speed increased and the fineness particles of $CaTiO_3$ were just obtained at 200 rpm speed at 1 h time due to agglomeration and the tendency of the particles to reduce the surface energy (Palaniandy and Jamil, 2009).

In fact, planetary mill operation involved the rotating disk and the vials either in the same direction (normal direction) or in the opposite direction (counter direction). Depending on the direction in which they move, the impact energy acquired by the balls varies. Figure 2.7 shows the XRD patterns of talc after ground in planetary ball mill at various grinding period.

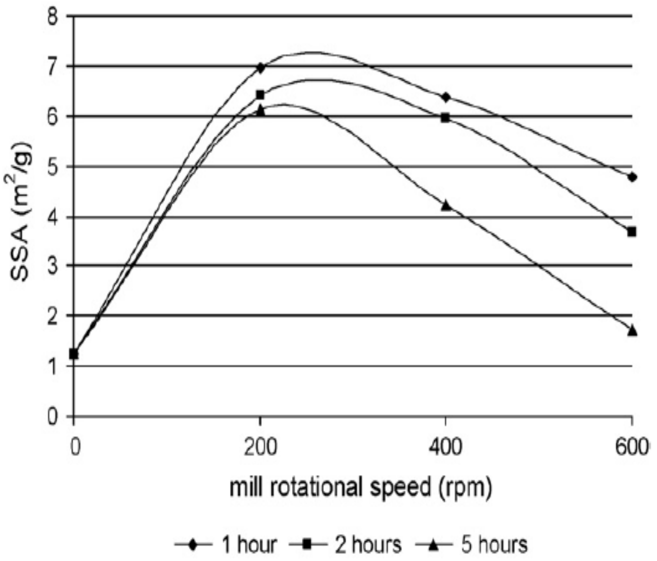


Figure 2.6: Change in specific surface area of calcium titanate ($CaTiO_3$) at various mill rotational speeds and grinding times (Palaniandy and Jamil, 2009)

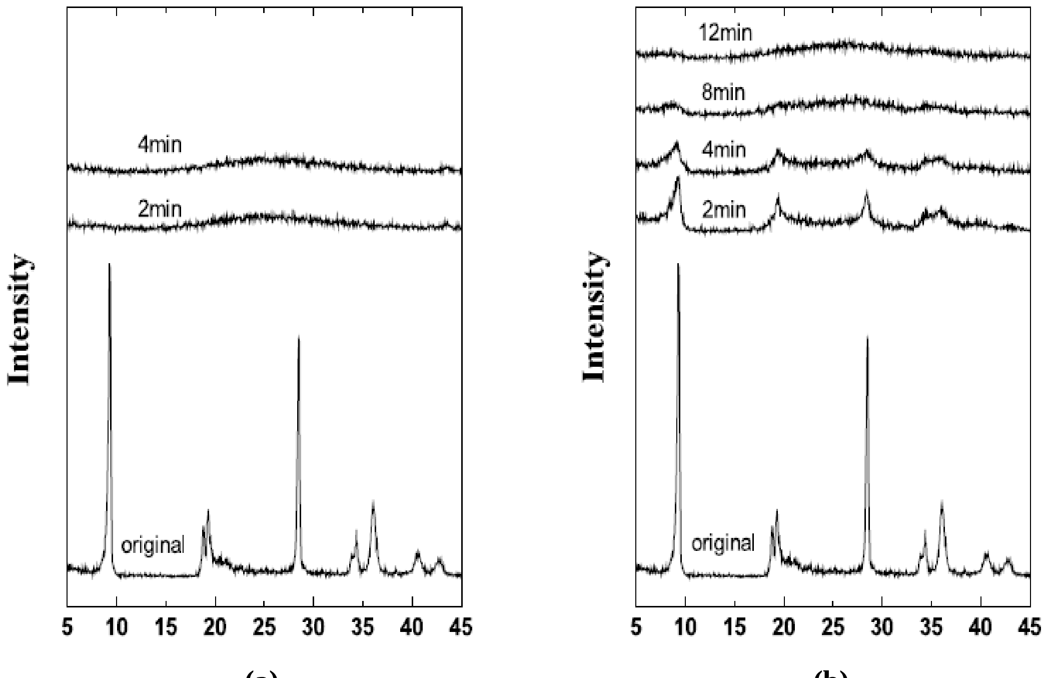


Figure 2.7: XRD patterns of the talc samples ground for various times; (a) counter direction; (b) normal direction (Mio *et al*., 2002)

The planetary mill which move in counter direction tends to changes the structure of talc to amorphous state sooner than normal direction. Thus, it was concluded that the rotation of the pot in the counter direction to the revolution is more effective in fine grinding especially for mechanochemical activation and mechanical alloying, due to promotion of the impact energy of the balls during grinding (Mio *et al*., 2002).

2.2.5 Grinding time

The grinding period is an important parameter as it determines the final size of the milled product. The grinding time required to reach a certain particle size varies depending on the mill rotational speed, the ball-to-powder ratio and the temperature inside the mill. However, the level of contamination will increase with grinding time and undesirable phases may form if the powder was ground for longer hours (Surayanarayana, 2004).

According to Stewart *et al*. (2003), during the initial stages of grinding a ceramic material, a reduction of the grain size occurs down to the limit of fragmentation, while further grinding can produce a phase transformation, a mechanochemical reaction, or recovery of the grains. In addition, by increasing the grinding time, the number of pulses increases and subsequently, more energy is transfer to the particles being ground (Pourghahramani and Forsberg, 2006a).

2.3. Effect of ultrafine grinding and characterizing methods on ground particles

The application of high energy grinding mill, such as planetary mill, allows dramatic changes in the structure and surface properties of solid materials. The most noticeable change with grinding is reduction in the particle size, generally to nanoscale. The mechanical treatment in a high-energy mill generates a stress field within the solids. Heat release can cause stress relaxation, the development of a surface area as a result of brittle fracture in the particles, generation of various sorts of structural defects, and stimulation of a chemical reaction within the solids (Palaniandy and Jamil, 2009).

Mechanochemical effect is another view of grinding, and now become a very important consideration in understanding of the properties of ground particles. Hence, the ground samples under high intensive grinding cannot be characterized by a particle size distribution alone and the characterization of particle morphology and structural changes where the mechanochemical were take place have to be considered.

2.3.1 Particle size reduction

Comminution, specifically refer to ultrafine grinding by high energy mill is known to produces ground particles with particle size below 10 µm (Jankovic, 2003). The particles in this size range exhibits several advantages such as magnetite with particle size <10 µm tend to improve the pigment qualities in terms of their colour, tinting strength, hiding power and oil adsoption (Legodi and Waal, 2007).

Basically, the effectiveness of ultrafine grinding in planetary mill is evaluated through determination of the final sizes of ground products. The evaluation included the analysis on the particle size and its distribution, as well as specific surface area, as there is an inverse relationship between surface area and particle size (Sanchez *et* *al*., 2004). The mean particle diameter (d_{50}), can be determined via surface area from BET measurement by using Equation 2.2.

$$d_{av} = 6/\sigma S \qquad \text{Equation 2.2}$$

where d_{av} is the equivalent spherical particle diameter (µm), σ is the density (g/cm^3) and S is the specific surface area (m^2/g) (Pourghahramani and Forssberg, 2006a; Subrt *et al*., 2000).

According to Pourghahramani and Forssberg (2006a)**,** for a given energy input, the d_{50} (mean particle diameter) value of hematite obtained from laser diffraction method are larger than the d_{av} (equivalent spherical particle diameter) of those determined from BET specific surface area as shown in Figure 2.8. This observation implies that pore agglomerates of primary particles are produced during intensive grinding. A small increase in d_{50} after intensive grinding also indicated the occurrence of agglomeration which is one of the main drawbacks of mechanical grinding.

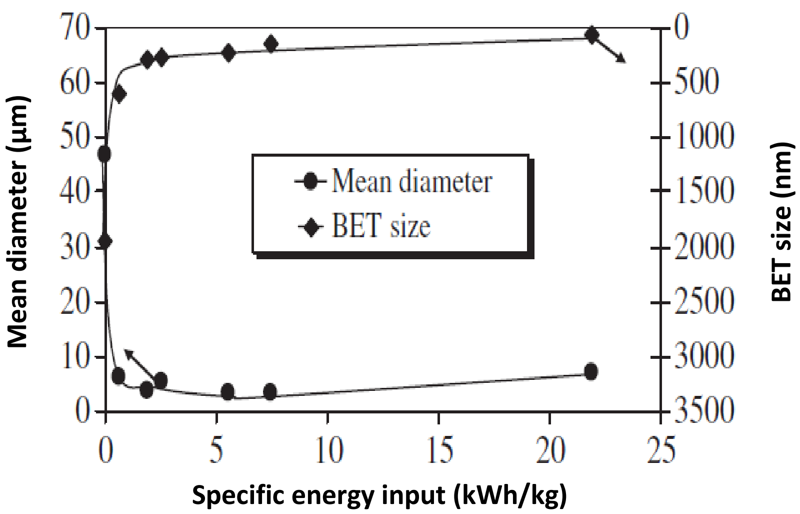


Figure 2.8: The mean particle diameter (d_{50}) and BET particle size as a function of specific energy input (kWh/kg) (Pourghahramani and Forssberg, 2006a)

2.3.2 Mechanochemical effect

Apart from inducing size reduction, the huge amount of energy delivered by the mill during high energy mill cause severe and intense mechanical action on the solid surfaces during fine grinding are known to lead to chemical and physicochemical effect in the near-surface region where solids come into contact under mechanical force. The mechanically initiated physicochemical effects in particles are generally terms as mechanochemical effect (Palaniandy and Jamil, 2009).

The consequence due to mechanochemical effect from structural distortion of crystal lattice during fine grinding had created much attention among researchers due to several advantages. These advantages include reduction in sintering temperature, increase in pozzolonic properties of cement filler, enhancement of leaching, production of nanocrystalline materials, improvement of reactivity of waste materials to be used as construction materials, transformation of phases, and production of new phase (Mahadi and Palaniandy, 2010; Chen, *et al*., 2007; Sanshez *et al*., 2004, 2007; Pourghahramani and Forssberg, 2006a).

As summarized Zhang *et al*. (2007), the mechanochemical phenomena are indicated by;

- formation of dislocation and point defect in the crystalline structure,
- mechanical activation of solid materials and,
- polymorphic transformation, amorphization, and crystallization.