Nanozeolite Produced by Wet Milling at Different Milling Time

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Abstract. Recently, there has been a considerable growing interest in utilizing nanozeolites due to their advantages over conventional micron sized materials. Zeolite particle may be reduced by mechanical treatment such as ball milling or grinding in order to get smaller particles. In this paper, effect of milling time on particle size and surface morphology of Zeolite were investigated by a few designed of experiments in aqueous environment. Zeta-sizer Nano series of particle sizer and Field Emission Scanning Electron Microscopy (FESEM) have been used to characterize this nanozeolite. Results shown that, there were changes of particle size and also the surface morphology of Zeolite.

1. Introduction

Zeolite is a large group of crystalline materials and have a framework of linked tetrahedral that consisting of four oxygen atoms around their cation. Zeolites are also known as molecular sieves and aluminosilicate materials that are characterized by their open structure of interconnected cavities that can be accessed by molecules, atoms and ions species [1]. The properties and uses of zeolites are being explored in many scientific disciplines: modern inorganic chemistry, physical chemistry, colloid chemistry, biochemistry, mineralogy, geology, surface chemistry, oceanography, crystallography, catalysis and in all types of chemical engineering process technology [2].

Ball milling treatment, as a cost-lowering and environmental friendly method has been used in this project at aqueous environment. Ball milling refers to the use of friction, collision, impingement, shear or other mechanical actions to modify the structures and properties of the Zeolite [3]. The reduction of the particle size of Zeolite causes larger external surface areas available for interaction, shorter diffusion path lengths reducing mass and heat transfer resistances in catalytic and sorption applications, decreasing of side reactions, enhancing selectivity as well as lowering tendencies to coke formation in some catalytic reactions [4].

Therefore, the objective of this study is to investigate the effect of milling time on particle size and surface morphology of Zeolite by wet ball milling treatment through Zeta-sizer Nano series of particle sizer and Field Emission Scanning Electron Microscopy (FESEM).
2. Methodology

2.1. Materials
The commercial powders of Zeolite was purchased from Fluka with means size about ≥45µm.

2.2. Ball Milling Treatment
Wet grinding has been selected in this study because it has some advantages over dry grinding such as the higher energy efficiency, lower magnitude of excess enthalpy and the elimination of dust formation [5]. The milling process was performed by mean of a planetary ball mill with some parameters that have been highlighted with respect to size reduction. Grinding time was varied for different experiment between 2 to 8 h while the rotational speeds were constant at 550 rpm for each experiment. All of the experiments were carried out in a 50 mL stainless steel jar with protective jacket of zirconium oxide and 2 mm of zirconium oxide balls were used for this milling process respectively. The grinding jar was set up and arranged eccentrically on the sun wheel of the planetary ball mill. The direction of movement of the sun wheel being opposite to that of grinding jars was selected with the ratio of 1: 1. A certain amount of Zeolite: 0.5 g, water: 10 ml and balls: 45 g were weighted accurately and placed in the jar at room temperature also at atmospheric pressure. The jar then sealed and imposed to milling. After milling, all sample were carried out then was allowed to be cooled down at 40˚C for 24 hours. Then all samples were continuing milling for 15 minutes and then were characterized.

2.3. Characterization
Particles size measurements were carried out using Zeta Nano Sizer S at 25 °C and the reading was taken at 173 ° scattering angle. Prior the measurement, 1 ml of nanosuspensions for each samples were taken out to introduced in the disposable cuvette to be measured. The samples were measured in triplicate. The dried powders were taken for FESEM analysis.

3. Results and discussion

3.1. Particle Sizer
The effects of milling time on particle size of Zeolite were investigated by a few designed experiments in aqueous environment and different time. The particle size distributions of all the Zeolite samples prepared were obtained by Zeta Nano Sizer S, as mentioned before. Figure 1 showed the influences of milling time on zeolite particle. The particle size without milling, the Z-average (mean value in nm) was 1889 nm then after milling treatment at 2 h the Z-average was 211.6 nm while for 4, 6 and 8 h were 185.2, 171.4 and 164.9 nm.

From original Zeolite it reduced about 88.80 % of particle size when imposed to milling time at 2 hours. Then, the particle size of Zeolite continuous to reduce when continuous imposed to milling process until 8 hours. 8 hours of milling time shown the smallest average of Zeolite particle size compared to others with reduction about 91.27% from the original size. From these sizes produced, we observed that the particles size is inversely proportional with grinding time. This closely related to the generation of energy over time during grinding process.

As we can see from figure 1, the shorter grinding time will produce larger mean particles compare to the longer grinding time. This result is consistent with the finding by Takatsuka et.al. [6] which found that the particles size reduce with increasing of running time of grinding. This can be understood from the interaction of particles and the grinding ball.
Interaction between frictional and impact forces due to the collision of ball and inner wall of jar which move at the difference speeds which will unleashes a high dynamic of energies. For a ‘nano’ process to take place, energy in the jar should be sufficient enough. Fadda et al [7] proposed that the particles breakage happen at initial stage of milling then equilibrium between re-agglomeration and de-agglomeration occur.

![Graph showing average particle size of Zeolite at different milling time.](image)

**Figure 1.** Average particle size of Zeolite at different milling time.

### 3.2. Surface Morphology

To study probable changes of morphology for ground powders of Zeolite after milling as well as to confirm the particle size results, all samples were subjected to Field Emission Scanning Electron Microscopy (FESEM). Some of the FESEM images of samples were shown in Figure 2. FESEM images indicated that almost in all samples, Zeolite powder with particles size less than 100nm may be recognise as a separated particle or in the form of larger agglomerates.

Amir Charkhi et al. [4] also reported the similar phenomenon when grinding Clinoptilolite by a wet ball milling treatment. Moreover most particles have lost their initial cubic shape(Fig.2a) and converted into spherical and also irregular shapes after imposed to the milling process with varied in milling times(Fig 2b,2c,2d,2e).

Moreover, Chunlong et al [8, 9] hypothesized that fractures or de-agglomerations easily happen at the defects, impurities and at the interface of the intergrowth within large Zeolite particles. Thus the mechanical stress that was generated by the jar ball mill randomly fractured or de-agglomerated the Zeolite particles into smaller fragment with varying size distribution and different morphology. The larger fragments were typically irregular shape whereas the small fragments tended to be spherical. From this observation of Zeolite morphology, we could summarize that FESEM results were in accordance with the characterization results by the particle size analyser that have been explained before.
Figure 3. The surface morphology of nanozeolite as a function of milling time: a) 0 h b) 2 h c) 4 h d) 6 h and e) 8 h
4. Conclusion
As a conclusion for this study we can conclude that at milling time 8 hours, the particle size is smaller than others while for surface morphology, we can observed that the nanozeolite tended to be spherical shape and also irregular shape after milling treatment. Therefore, ball milling is a powerful mechanical method to reduce size of Zeolite particles. We proposed that, the condition of milling should be carefully selected to get the nanozeolite powder.

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