Wet gringing of zeolite in stirred media mill

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Abstract. In the present study the results of systematic experimental series are presented with the specific goal of optimizing the zeolite nanoparticles’ production using a wet stirred media mill. The diameter of the grinding media as well as the rotor velocity were varied in the experiments. Particle size distribution and “outer” specific surface area of the ground samples were measured by a laser particle size analyser. Additionally, BET, XRD and FT-IR analyses were performed for the characterization of the “total” specific surface area as well as the crystalline and material structure, respectively. Based on the results of the laboratory experiments it was found that wet stirred media milling provided significant reductions in the particle size of zeolite. Furthermore, the crystallinity of the samples also decreased, so not only the physical but the mineralogical characteristics of zeolite can be controlled by stirred media milling.

1. Introduction
Zeolites are natural crystalline aluminosilicates. Structurally, zeolites are tectosilicates exhibiting an open three-dimensional structure containing cations needed to balance the electrostatic charge of the framework of silica and alumina tetrahedral. To collapse of the crystal structure can be desired in some cases since different strength of Bronsted and Lewis acid and base sites can thus be obtained [1, 2]. This, in turn, can provide a better catalytic performance [3].

Ion-exchange properties of zeolites can be utilized in agriculture because of their large porosity and high cation-exchange capacity[4]. They can be used as both carriers of nutrients and a medium to free nutrients [5]. Zeolite incorporation in soil was found to increase crop yields and to promote nutrient use efficiency [6]. Other possible uses being investigated include applications as a carrier of slow-release fertilizers, insecticides, fungicides, and herbicides, and as a trap for heavy metals in soils. [7]

Stirred media mill is a high energy density mill belonging to the group of drum mills, which is used for industrial nanosize particle production in wet mode. Stirred media mill is an important milestone in the mill development, because while before the movement of the grinding media was carried out by the rotation (ball mill) or vibration (vibration mill) of the milling chamber, in this case the rotation of the concentrically or eccentrically placed rotor makes the grinding media moved. As a result, the grinding balls colliding with each other; are pressed to the mill liners; and colliding with the rotor. The particles of the feed material are fractured by the impact, pressure, collide and friction stresses [8].

Stress model are widely used for the description of the stirred media milling. Using the product related stress model described by Kwade et al. [9], the specific surface area or the particle size can be related to the operation parameters, thus creating the purposeful control of the product of the stirred media mill. The degree of stress energy has an optimum. When the energy input is high enough to
fracture the agglomerates or particles into smaller ones by only one stress event, the optimum stress energy is achieved.

Stirred media mills can be used for a lot of various aims besides the ultrafine grinding. One is the mechanochemical activation of the materials due to the high energy density in the milling chamber, this was presented by Mucsi et al [10]. Stirred media mills can also be used in dry or wet mode. In dry mode, fundamentals of particle rounding and surface roughness reduction was revealed by Racz [11].

2. Materials

Natural zeolite used in this study originated from Măd deposit, Hungary. Its main mineral components were identified as clinoptilolite, cristobalite, smectit by XRD pattern. The natural zeolite was preliminary crushed and ground resulting in a maximum particle size less than 150 µm.

Table 1. Chemical composition of natural zeolite used in the experiment (in w/w%, dry basis)

| Oxides   | w/w% | Elements | ppm |
|----------|------|----------|-----|
| SiO₂     | 74,7 | Cu       | 6   |
| Al₂O₃    | 13,2 | Zn       | 67  |
| MgO      | 0,96 | Pb       | 44  |
| CaO      | 1,54 | Rb       | 194 |
| Na₂O     | 0,19 | Sr       | 437 |
| K₂O      | 1,53 | Ba       | 143 |
| Fe₂O₃    | 1,54 | Cr       | >5  |
| MnO      | 0,035| Co       | >5  |
| TiO₂     | 0,092| Ni       | >5  |
| P₂O₅     | 0,017| Zr       | 182 |
| ∑        | 93,834|          |     |

From the chemical composition of natural zeolite (measured by Rigaku XRF apparatus) used in the experiment can be seen the main components are SiO₂, Al₂O₃ and MgO (Table 1). The SiO₂/Al₂O₃ ratio is 5,66.

3. Methods

The experiments were carried out in a stirred media mill (Netzsch MiniCer) in circular mode. During the experiments the particle size distribution F(x) and the „outer” specific surface area of the ground samples were measured and calculated by a laser particle size analyzer, the energy consumption of the mill was measured, and then the specific grinding energy was calculated. Additionally, the BET Surface Area (m²/g), the mineral composition by XRD and the material structure by FT-IR analyses were performed for the characterization of the „total” specific surface area as well as the crystalline and material structure, respectively.

3.1 Particle size distribution

During the milling, the particle size distribution of the ground samples was determined by a Horiba LA-950V2 laser diffraction particle distribution analyzer in distilled water media. Before the measurement, ultrasonic treatment was applied for 1 min and 0.5 mL sodium pyrophosphate was used in a 50 gL⁻¹ concentration for best dispersion. Samples were taken after 1, 3, 5, 10, 15, 30, 60,
90, 120, 150 and 180 min grinding. For these samples the calculated specific surface area was also measured by the Horiba LA-950V2 laser diffraction particle distribution analyzer.

3.2 Specific surface area by BET method
For the measurement of the total specific surface area Tristar 3000 from Micrometrics Corporation was used. Before each measurement the sample has to be degassed. From the adsorbed gas the surface area of the particle is determined. The BET (Brunauer, Emmett and Teller) method is used to determine the surface area of the particles. To prepare the samples for the BET measurement, the suspensions were dried overnight in a laboratory oven at 100°C. To degas the powder the samples were dried at 90°C for 30 minutes and additionally at 300°C for 180 minutes in flowing nitrogen gas in the Micrometrics Smartprep before the adsorption measurements were carried out. The complete adsorption-isotherms were recorded. The specific surface area was calculated by a 5 point Brunauer-Emmett-Teller (BET) method. The weight of each sample was approximately 1 g.

3.3 X-Ray powder diffraction (XRD)
XRD investigations were carried out on a Bruker D8 Advance diffractometer (Cu-Kα radiation, 40kV, 40mA) in parallel beam geometry obtained with Göbel mirror (0.6 mm exit slits, 2.5° axial Soller), equipped with Vantec-1 position sensitive detector (1° opening, 2.5° axial Soller). Measurements were recorded in 2-70°(2θ) range of angle with 0.007°(2θ)/28 secundum goniometer speed. Crystalline components were identified by Search/Match algorithm in Bruker DiffracPlus EVA software package using ICDD PDF-2 (2005) database. Quantitative results were obtained by Rietveld-refinement, in Bruker TOPAS4 software using ICSD database, unit cell parameters were refined and mean crystallite sizes determined.

3.4 FT-IR
To follow the structural changes due to grinding process Fourier Transformed Infrared Spectroscopic measurements of zeolite carried out by JASCO FT-IR 4200 type Fourier Transformed Infrared Spectrometer in Reflection mode, diamond ATR PRO470-H condition was used. 3 spectra was made from each samples. For making of one spectra of a sample, different parts of zeolite was measured. One spectra averaged of 64 FT-IR measurements with 4 cm⁻¹ resolution number.

4. Experimental
The grinding experiments were carried out in a stirred ball mill (Netzsch MiniCer) in wet mode, using 180 min maximum grinding time. The first experimental serie is based on the influence of the circumferential velocity of the rotor, which was studied at 7.7, 9.3 and 10.8 m/s, and the second one is that of the grinding media size which was studied at 550 µm, 700 µm and 900 µm. All other grinding operating parameters were permanent. The suspension concentration was 10 w/w %.

5. Results
Figure 1 shows the particle size analysis results of the 180-min-ground final products. It shows the frequency curves. It can be observed that bimodal nature of the feed remained after grinding, but significantly shifted to the submicron size range. The finer mode of all of the ground products were finer than 200 nm, on the other hand the coarser mode was 2 µm approximately. Consequently, since the initial modes were 3 µm and 50 µm, not only the surface roughness of the particles was changed but breakage of the particles was occurred due to the grinding process.
Figure 1. Frequency distribution of zeolite final product

Figure 2. The calculated specific surface area as a function of the specific energy

Figure 2 shows the produced specific surface area of the ground samples during grinding to monitor the grinding kinetics. It shows the calculated specific surface area as a function of the specific energy input. From this point of view it can be seen that using the largest grinding media size resulted in the lowest specific surface area. To observe more significant difference in the effect of the operating parameters stress models were applied.

Figure 3. The product fineness as a function of the stress number

Figure 4. The median size as a function of the specific energy

Figure 3 shows the product fineness (median size) as function of the stress number for different grinding media size and circumferential velocity. Based on the relation of these parameters it can be established that grinding occurred with sufficient size of grinding media since the stress energy is sufficient to break the particles at the beginning of the grinding process.
Figure 4 shows the median size as function of the specific grinding energy. The main difference is given by the bigger grinding media size. In order to find the optimal stress intensity this figure can be used. It can be estimated in two ways. First way is to read the different values of the specific grinding energy which contains to an exact median size. In this case the 500 nm of median size was chosen.

**Figure 5.** Specific grinding energy required to produce a median size of 500 nm as function of stress intensity

**Figure 6.** The product fineness at 3000 kJ/kg specific energy as a function of the stress energy

If the specific grinding energy required to produce a median size of $x_{50} = 500$ nm is constant as function of stress energy, the relation is shown in figure 5. At lower stress intensity high specific energy is necessary to produce a median size of 500 nm, because the stress intensity is too low for an effective grinding and therefore a large number of stress events are necessary. Therefore, in this range of stress energy the specific energy required for a certain product fineness decreases with increasing stress intensity. If the stress intensity is so high, that is average the feed particles can be broken, the specific grinding energy reaches a minimum value. If the stress energy is increased further, the energy utilization of each stress event decreases, so that with increasing stress intensity more specific grinding energy is required to produce a median size of 500 nm. The optimum stress intensity is $0.1 \times 10^{-3}$ Nm to produce a median size of 500 nm.

Besides the specific grinding energy at a constant product fineness, also the product fineness at a constant specific grinding energy input can be presented as a function of the stress intensity. In figure 6 the median size is produced at a specific energy input of 3000 kJ/kg are depicted as a function of the stress intensity. According to literature, for single particle stressing, the maximum energy utilization and thus, the optimum stress intensity can be found at fracture probabilities of 100 % [12]. The minimum median size is 300 nm.
If the optimal stress energy is $0.1 \cdot 10^{-3}$ Nm and the grinding time is 180 min, the produced specific surface area (which was measured by BET method) as a function of the SE/SE$_{opt}$ optimum is presented in figure 7. It can be seen that the SSA increased until the ratio reached the optimum value, then it began to decrease.

The results of the XRD measurements of the feed sample and the 180 min ground samples show that amorphization occurred due to grinding (figure 8). Significant amorphization was detected since the content of amorphous phases in the feed material was only 7% which increased to 36% up to 50% in the ground products (depends on the circumstances). The ratio of clinoptilolite phase parallel decreased due to grinding.

In figure 9, the results of the 180-min-ground zeolite samples’ FT-IR measurement in transmission mode can be seen. The feed (which is the first curve from the top) had the highest intensity of the 790 cm$^{-1}$ peak related to the AlO$_4$ vibrations, and it was reduced significantly due to the effect of grinding. New peaks were appeared at 1472, 1098, 874 and 856 cm$^{-1}$. 1472 cm$^{-1}$ is assigned to the stretching
vibration (O–C–O), 1098 cm\(^{-1}\) is assigned to the asymmetric stretching vibration (T–O–Si, T=Si or Al), 874 and 856 cm\(^{-1}\) are assigned to the Si–O stretching, OH bending (Si–OH). Other peaks were disappeared due to grinding: at 1045 and 696 cm\(^{-1}\). 1045 cm\(^{-1}\) is assigned to the asymmetric stretching vibration (T–O–Si, T=Si or Al), 696 cm\(^{-1}\) is assigned to the symmetric stretching vibration (Si–O–Si and Al–O–Si) [13]. These changes indicate the structural changes due to grinding.

![Figure 9. The results of the 180-min-ground zeolite samples’ FT-IR measurement](image)

6. Conclusions
Based on the results of the laboratory experiments it was found that the optimum stress intensity is \(0.1 \cdot 10^{-3}\) Nm to produce a median size of 500 nm. The optimum stress intensity is \(0.07 \cdot 10^{-3}\) Nm to produce minimum median size product at 3000 kJ/kg specific energy. It can be seen that the SSA - BET increased until the SE/SE\(_{opt}\) reached the optimum value than it began to decrease. The changing of intensity of FT-IR peaks indicates the structural changes due to grinding. Furthermore, the crystallinity of the samples also decreased.

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References
[1] Xie J, Kaliaguine S. 1997 Appl Catal A Gen 148 415–23. doi:10.1016/S0926-860X(96)00234-7.
[2] Zielinski P a., Van Neste a., Akolekar DB, Kaliaguine S. 1995 Microporous Mater 5 123 doi:10.1016/0926-6513(95)00050-J.
[3] Akçay K, Sirkeciöğlu A, Tather M, Savaşçı ÖT, Erdem-Şenatalar A. 2004 Powder Technol 121 doi:10.1016/j.powtec.2004.03.012.
[4] Reháková M, Čuvanová S, Dzivák M, Rimár J, Gaval’ová Z. 2004 Curr Opin Solid State Mater Sci 8 397–404. doi:10.1016/j.cossm.2005.04.004.
[5] Misaelides P. 2011 Microporous Mesoporous Mater 144 15 doi:10.1016/j.micromeso.2011.03.024.
[6] Malekian R, Abedi-Koupai J, Eslamian S S 2011 J Hazard Mater 185 970 doi:10.1016/j.jhazmat.2010.09.114.
[7] Ramesh K, Reddy DD. 2011 *Adv. Agron* **113** 219 doi:10.1016/B978-0-12-386473-4.00004-X.
[8] Rácz Á. Research and development of the grinding process for the production of ultrafine materials. PhD Thesis, University of Miskolc, 2014. http://www.doktori.hu/index.php?menuid=193&vid=12807
[9] Breitung-Faes S, Kwade A. 2008 *Chem Eng Res Des* **86** 390 doi:10.1016/j.cherd.2007.11.006
[10] Mucsi G, Rácz Á, Mádai V. 2013 *Powder Technol* **235** 163 doi:10.1016/j.powtec.2012.10.005
[11] Rácz Á. 2014 *Chem Eng Technol* **37** 865 doi:10.1002/ceat.201300671
[12] Kwade A. 2004 *Int J Miner Process* **74** S93 doi:10.1016/j.minpro.2004.07.027
[13] Panias D, Giannopoulou IP, Perraki T 2007 *Colloids Surfaces A Physicochem Eng Asp* **301** 246 doi:10.1016/j.colsurfa.2006.12.064