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COMPARATIVE INVESTIGATION OF ZEOLITE GRINDING IN STIRRED MEDIA MILL AND PLANETARY BALL MILL

ABSTRACT

Zeolites are porous materials which can be used in the treatment of wastewater or polluted air for instance. In order to increase their adsorption capacity and make them even more effective for this application, zeolites can be mechanically activated by grinding. This process may lead to changes in particle size distribution, material structure, morphology, and specific surface area, depending on the grinding time and the type of mill that would be used for this operation. Thus, the aim of this study is to compare the changes occurring in a natural Hungarian zeolite when dry-ground in stirred media mill and planetary ball mill for different times. At the same time, the energy efficiency of both types of mill was also compared. The particle size distribution as well as the outer specific surface area of the materials obtained after each grinding were characterized with a Laser Particle Size Analyzer. The structure and particle morphology of the obtained materials were also observed using Fourier-Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The total specific surface area was analyzed with a BET Specific Surface Area and Porosity Analyzer.

Keywords: zeolite, mechanical activation, energy efficiency, stirred media mill, planetary ball mill, material characterization

Introduction

Zeolite is the denomination for a category of around 40 different rock types from volcanic origin and constituted of a crystalline aluminum hydrosilicate network. This type of mineral is ordered in 3-Dimensional silica-alumina (SiO_4-AlO_4) tetrahedra connected by shared oxygen atoms, forming a honeycomb-like framework. This framework combined to the overall negative charge of the net gives rise to important adsorption and cation-exchange propertiesof zeolite.

Due to these properties, zeolites are used in various fields, mainly in agriculture, in order to increase the nutrient uptake efficiency, but also in the construction field to replace a part of cement and make it more sustainable and durable [1]. Another important domain where the unique properties of zeolites can be used is in the treatment of water, be it to remove heavy metals, hazardous ions or industrial dyes [2]. Similarly, a layer of zeolite can be added to biofilters in order to treat polluted air by trapping, then destroying volatile organic compounds [3].

In order to further improve zeolite's properties, Bohács et al [4] have shown that mechanical activation by fine-grinding in a stirred media mill seems to be an efficient solution. What this means is the comminution under 50 μm of the material leads to property changes, like higher specific surface area, modified particle size distribution, and new structure. These changes can be reached by high energy density mills like the planetary ball mill or the stirred media mill. The difference between these, besides the structure of their apparatus, is their maximum achievable acceleration, which is lower for the planetary ball mill. However, due to its ability to be used in inert atmosphere, planetary ball mill is usually used to produce small quantities of materials for high-tech application, while the stirred media mill is mainly used for high scale processes. One disadvantage of the latter, however, is its sensitivity for aggregation, which could be problematic to a certain extent [5].

So the aim of our research is to grind a natural zeolite in two different mills for various times and compare the properties of the end products as well as the energy efficiency of both mills. Thus, we can decide which mill type would be better to get the highest added value zeolite for applications in treatment processes.

Materials and methods

Material

The natural zeolite used in the following study comes from the Hungarian Rátka deposit. It is mainly constituted of clinoptilolite. The particle density of the zeolite is 1.91 g/cm^3 and its bulk density is 0.445 g/cm^3. Before grinding, the feed material was sieved under 100 μm, with a median particle size of 16.9 μm.

Methods

Mechanical activation by grinding

For the mechanical activation of zeolite, a stirred media mill set in horizontal configuration and in dry and batch mode, as well as a planetary ball mill in dry mode, were used.

In the case of the laboratory stirred media mill, the useful volume of the mill was 530 cm^3, 70 % of which was filled with the 0.8 – 1 mm sized zirconium silicate ceramic grinding balls. The chosen material filling ratio was 50 %.The rotor circumferential velocity of the mill was 6 m/s. The different grinding times analyzed in this experiment were 1 min, 3 min, 5 min, 10 min, and 20 min. After grinding, the balls and the zeolite were separated on 500 μm sieves.

The grinding experiments were repeated by Fritsch Pulverisette 5 Premium line high energy density planetary ball mill. For the mechanical activation two 150 ml grinding bowls were used with zirconium oxide balls and a diameter of 5 mm. Each bowl was filled with 30 g zeolite and 150 g grinding balls, the circumferential velocity and the grinding times were the same as for the stirred media mill. After each grinding experiment, the energy used by the mill was also noted.

Particle size distribution and geometric specific surface area

The particle size distribution and the “outer” (geometric) specific surface area of the obtained ground products were determined by a HORIBA LA-950V2 laser particle size distribution analyzer. The material was dispersed in distilled water with 1 mL sodium pyrophosphate, and ultrasonic treatment was applied during the measurements to improve the dispersion of fine particles. From the measured data, the particle size distribution was calculated based on the Mie-theory by using clinoptilolite refractive index, and the geometric specific surface area was calculated by the same device using shape factor 1.0 (Heywood factor).

Specific surface area by BET

Micrometrics VIII Gemini type BET specific surface area analyzer was used to get more information about specific surface area (SSA). The sample preparation include the degassing in ultra-high purity nitrogen for a night at 105°C to remove the adsorbed water. The SSA was determined by a 5-point BET measurement with nitrogen.

FTIR

Structural changes were analyzed by Fourier Transform Infrared (FTIR) Spectroscopy, in order to detect the vibrations of chemical bonds within the material. A JASCO FTIR 4200-type Fourier Transform Infrared Spectrometer was utilized for this purpose, which was set in reflection mode with a diamond ATR PRO470-H. The background spectrum was recorded at room temperature with empty cell. The spectrum for each sample was measured from 400 cm^{-1} to 4000 cm^{-1} using a Perkin-Elmer spectrum, which determines the absorption spectrum of the samples. Each spectrum was baseline corrected.

Microstructural analysis by SEM

In order to observe the morphological changes of particles (shape and size) after grinding, Phenom ProX electron microscopy equipped with EDS detector was used. The sample preparation included the dispersion of ground zeolite particles on a carbon stick placed on an aluminum sample holder. Elemental analysis of the sample was performed by using accelerating voltage of 15 kV.

Results and discussion

Mechanical activation by grinding

In order to compare the energy consumptions of the stirred media mill and planetary ball mill, the specific grinding energies for each grinding experiment were computed, and the median particle sizes and 90 % passing sizes (d_{90}) obtained after each grinding were plotted as a function of the calculated values, as shown on Figure 2. Figure 1 shows the cumulative particle size distributions obtained for each ground product. The first point of each curve corresponds to a grinding time of 1 min, the second point is the 3 min grinding, the third is 5 min, the fourth point corresponds to 10 min, and the fifth is the 20 min grinding.

What can be seen in this Figure is the high effectiveness of the stirred media mill compared to the planetary ball mill under the given circumstances. Indeed, stirred media mill gives finer particles with a lower specific energy. For one grinding experiment with a defined grinding time, the planetary ball mill requires almost 4 times more energy while giving coarser particles. A significant example of that is the 20 min grinding experiment, which is represented by the last point of each curve on Figure 2. In this case, the d_{90} obtained with the stirred media mill is 17.47 μm with 7189.08 kJ/kg, and for the planetary ball mill, the d_{90} was 47.27 μm, which is about 3 times coarser, with an energy of 25 800.00 kJ/kg.

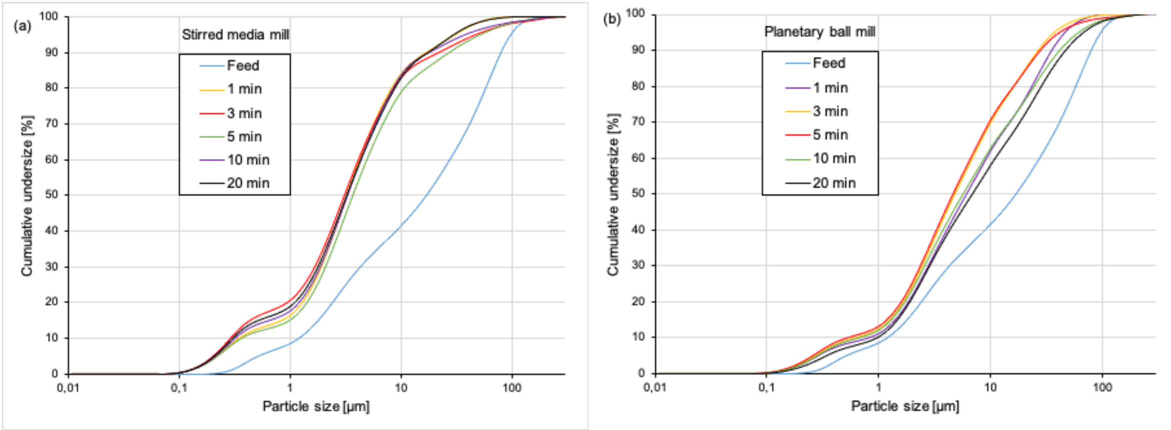

Figure 1

Particle size distribution of the zeolite feed and the products after different grinding times for the stirred media mill (a) and the planetary ball mill (b).

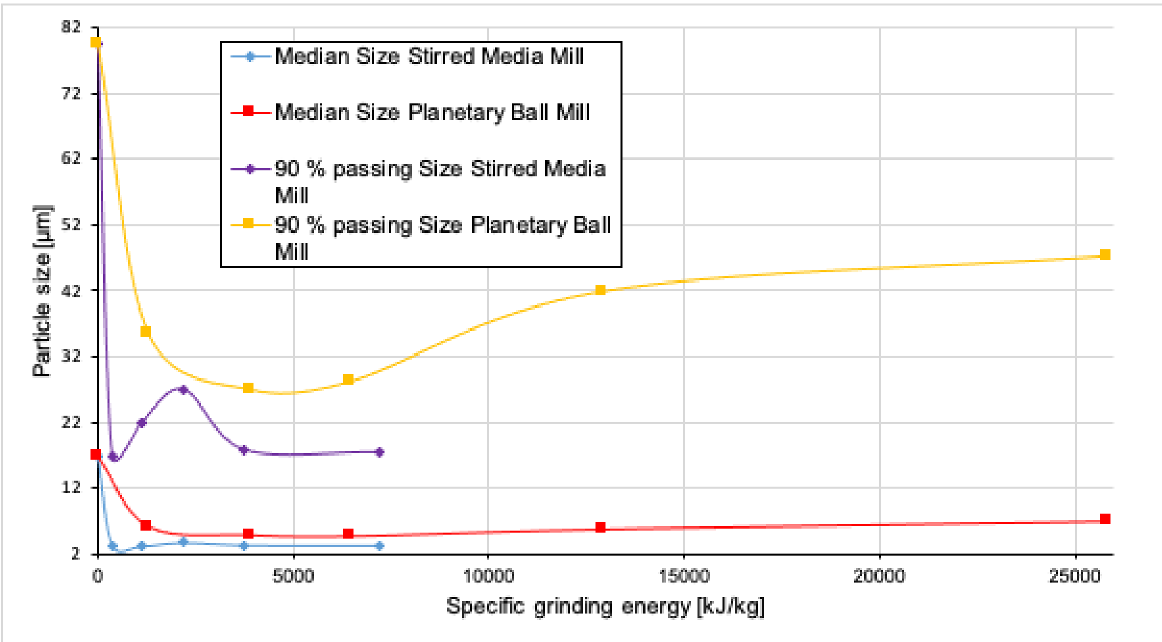

Figure 2

Median particle size and d_{90}as a function of the specific grinding energy for stirred media mill and planetary ball mill.

Particle size distribution and geometric specific surface area

Figure 1 shows the cumulative particle size distribution for both mills. For the stirred media mill, a significant decrease of the particle size can already be noticed at 1 min. While the d_{90} for the zeolite feed was 79.66 µm, it dropped to 16.87 µm at 1 min, and stays between 17 µm and 28 µm for the next grindings. As for the planetary ball mill, we can see that the particles become finer until 5 min, then they start aggregating, leading to the curves coming closer to the feed's curve. Indeed, in this case, the finest d_{90} is obtained after 3 min, with 26.91 µm, which then increases up to 47.27 µm after 20 min.

The median particle size and the d_{90} after each grinding and for each mill are presented in Figure 3. This clearly shows a size diminution phase and an aggregation phase. For the case of the planetary ball mill, it can be seen that the 1 min and 3 min grindings give a particle size decrease, and longer grinding times result in an aggregation phenomenon. On the other hand, the stirred media mill has 2 patterns: The first minute of grinding gives a particle size reduction and particles then rapidly aggregate until the 5 min grinding. After 10 min, the particle size decreases again before stabilizing.

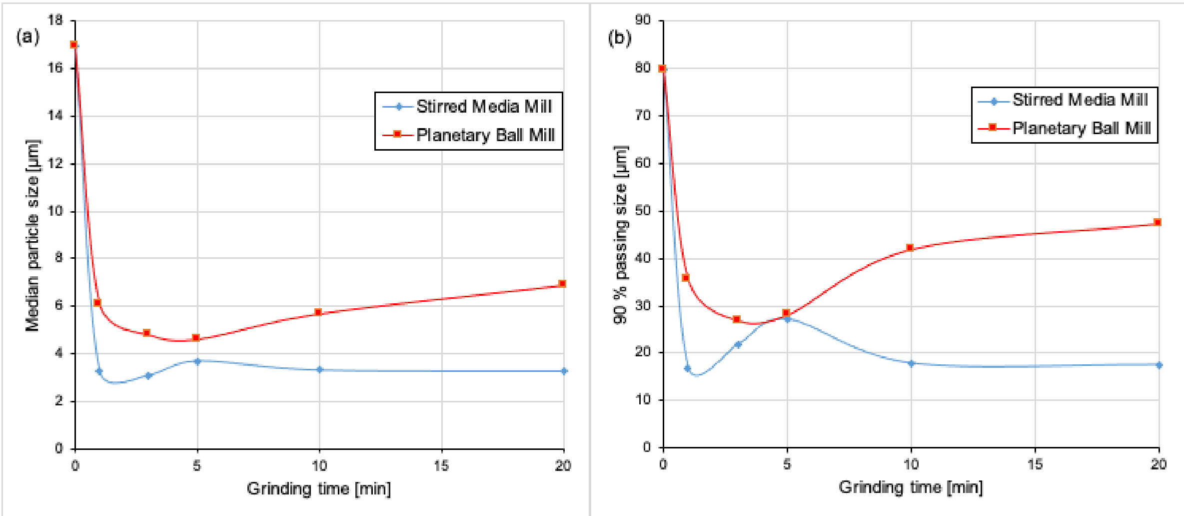

Figure 3

Median particle size (a) and d_{90} (b) comparison for stirred media mill and planetary ball mill at different grinding times.

The plot of the geometric specific surface areas (SSA) obtained after each grinding can be seen on Figure 4. Here, the geometric SSA for the stirred media mill experiments is clearly higher than those of the planetary ball mill. The highest SSA is obtained with the stirred media mill, before the aggregation phase, so before 5 min. The highest value we got was for the 3 min grinding, with 2.91 m^2/g, the feed's SSA being 1.06 m^2/g. In comparison, the highest value we got with the planetary ball mill was at 5 min with 19 055 cm^2/g, which is around 1,5 times smaller than the highest value obtained by stirred media mill. From these experiments and the related patterns, it seems like the best material can be obtained by mechanically activating the zeolite feed in a stirred media mill between 1 min and 5 min.

So, the natural Hungarian zeolite sieved under 100 µm, when dry-ground with a horizontal stirred media mill, gives fine particles with a median size as small as 3.10 µm after 3 min of grinding with a specific grinding energy of 1092.01 kJ/kg. After grinding for 20 min, the particles obtained had a median size of 3.25 µm and the energy consumed was of 7189.08 kJ/kg.

When the zeolite material was dry-ground in a planetary ball mill, it gave larger particles compared to the stirred media mill, the smallest median particle size being 4.63 µm after 5 min of grinding with an energy of 6450.00 kJ/kg, compared to 2184.02 kJ/kg for the stirred media mill for the same grinding time. The planetary ball mill ended up giving particles with a median size of 6.89 µm after 20 min using 25 800.00 kJ/kg, which is 2 times coarser particles for 3.5 times as much energy.

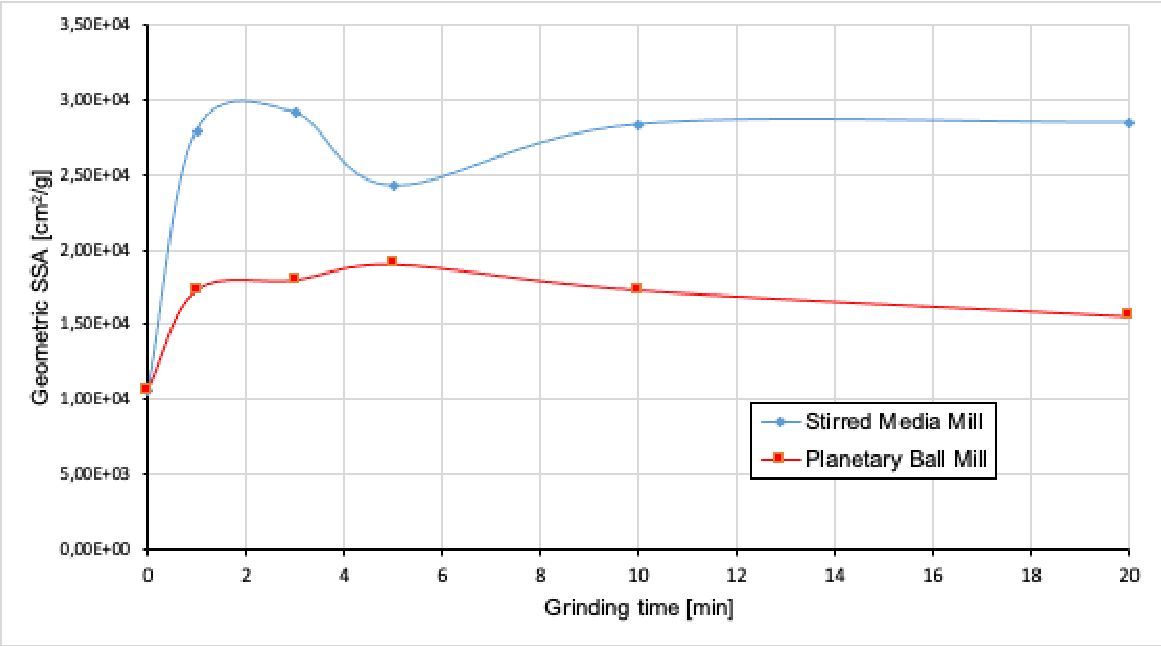

Figure 4

"Outer" (geometric) specific surface area (SSA) comparison for the stirred media mill and the planetary ball mill after different grinding times.

Specific surface area by BET

In Figure 5, we can find the plot of the total SSA of the stirred media mill and the planetary ball mill products. The curve for the stirred media mill looks very similar to the one in Figure 4: It starts with a rapid increase from a total SSA of 25.17 m^2/g for the feed material to 32.75 m^2/g after 3 min of grinding, then we see it decrease to 26.30 m^2/g at 5 min, before increasing again up to its maximum value, 49.09 m^2/g for the 20 min grinding product. This value is almost twice as high as the SSA of the feed zeolite. However the planetary ball mill shows a different behavior. After grinding the zeolite material for 1 min in the planetary ball mill, the total SSA value decreases to 23.81 m^2/g before increasing again until a maximum value of 38.31 m^2/g at 10 min. The total SSA then slowly sinks again due to the aggregation phase, reaching 30.23 m^2/g after 20 min.

So, the results obtained with BET for the stirred media mill products are in accordance with the previous observations. As for the planetary ball mill results, they are in good agreement with the different phases of comminution and aggregation observed before.

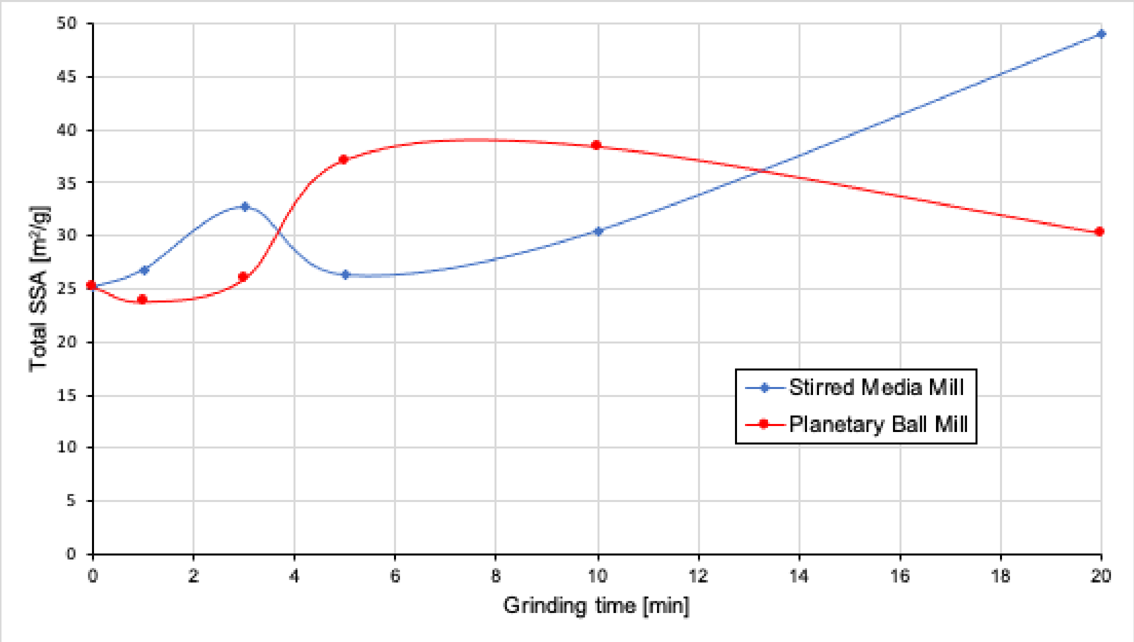

Figure 5

Comparison of the total specific surface areas obtained with BET as a function of the grinding times.

FTIR

The FTIR analysis of the ground zeolite gives the spectra presented in Figures 6 and 7. The spectrum shows that the wide overlapping absorption band between 3650-3000 cm^{-1} centred at 3420 cm^{-1} is related to the outer surface chemical groups of the clinoptilolite (clp) crystal structure that is associated with the stretching vibrations caused by O-H. Next to this broad band a small sharper peak at 3630 cm^{-1} is attributed to the O-H stretching vibration of water in illite. The peak observed at 1630 cm^{-1} is related to bending and stretching vibrations of H-O-H bond in surface adsorbed molecular H_2O. The absorption band between 950-1260 cm^{-1} regions result from the bending and stretching vibrations of Si-O or Al-O bonds in the clinoptilolite structure. This band centred at ~ 1000 cm^{-1} and the position of this band depends on the Al/Si ratio. The band located at about 420-500 cm^{-1} is assigned to a T-O bending mode.

To compare the FTIR spectrum of the zeolite ground in stirred media mill and planetary ball mill it can be observed that the intensity of peaks are changed with grinding. This may be the result of a change of particle size, as the signal amplitude increases with a decrease in particle diameter. So, the results are well correlated with the laser particle size analysis. However, no phase change could be observed here.

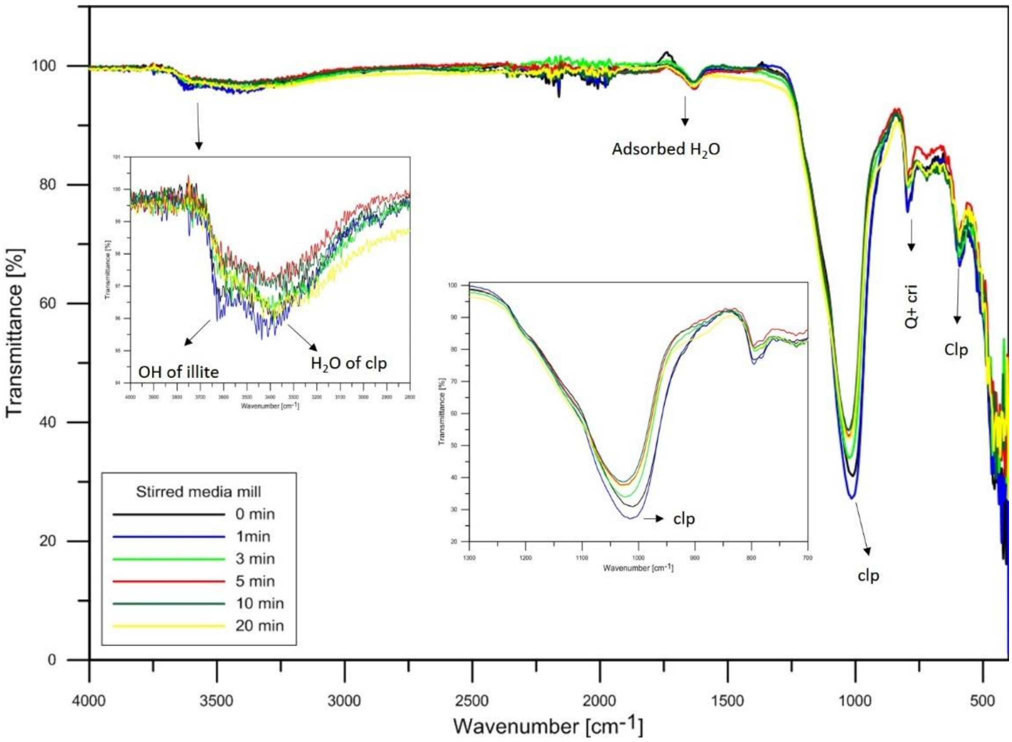

Figure 6

FTIR spectrum of the stirred media mill products.

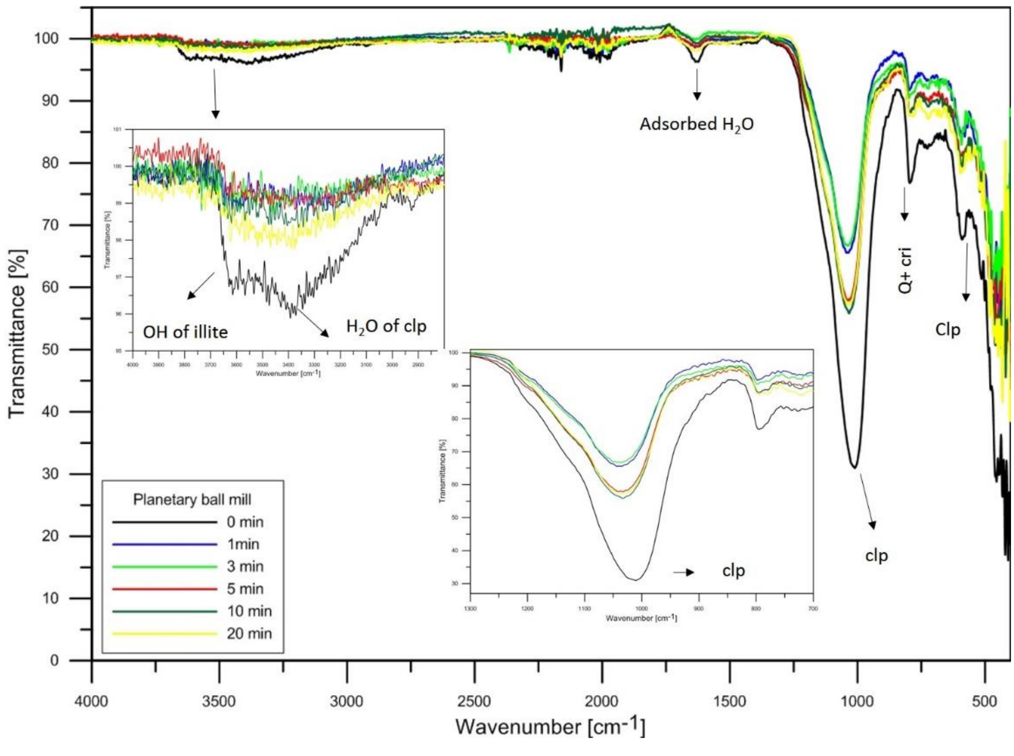

Figure 7

FTIR spectrum of the planetary ball mill products.

Microstructural analysis by SEM

With SEM, we can compare the morphology of the particles in each product. The EDS detector analyzed the elemental composition of the products as well: The major elements were Aluminum and Silicon, but Sodium, Potassium, Calcium and Magnesium also occur in low amount. These are all the species originally present in the mineral, which indicates that there was no contamination caused by the grinding.

As for the microstructure, the feed material contains large angular particles, as seen in Figure 8 a). From the scale on Figure 9 a), we could see that the particles are all less than 100 µm, as they were sieved before the experiments.We can also note that the size distribution seems very wide, as we can see tiny particles and much larger particles, which is in correlation with the previous results from particle size analysis.

In Figures 8 and 9, the images b) correspond to the 1 min grinding product, c) to the 3 min one, d) is the image after 5 min of grinding, e) corresponds to 10 min of grinding and f) is the product after 20 min.

When we look at the products of the stirred media mill on Figure 8, the tendency underlined with the laser particle size analysis is encountered again: The particles become smaller and smaller until Figure 8 d), so until 5 min of grinding. Then, on the Figure 8 e) and f), which correspond to 10 min and 20 min of grinding, aggregates are clearly visible, as smaller particles have piled up into irregular coarse ones. Another particularity we can notice is the shape of the particles, as they tend to have smoother edges throughout the different grinding experiments, except for the Figure 8 e), the 10 min grinding, which shows harsher

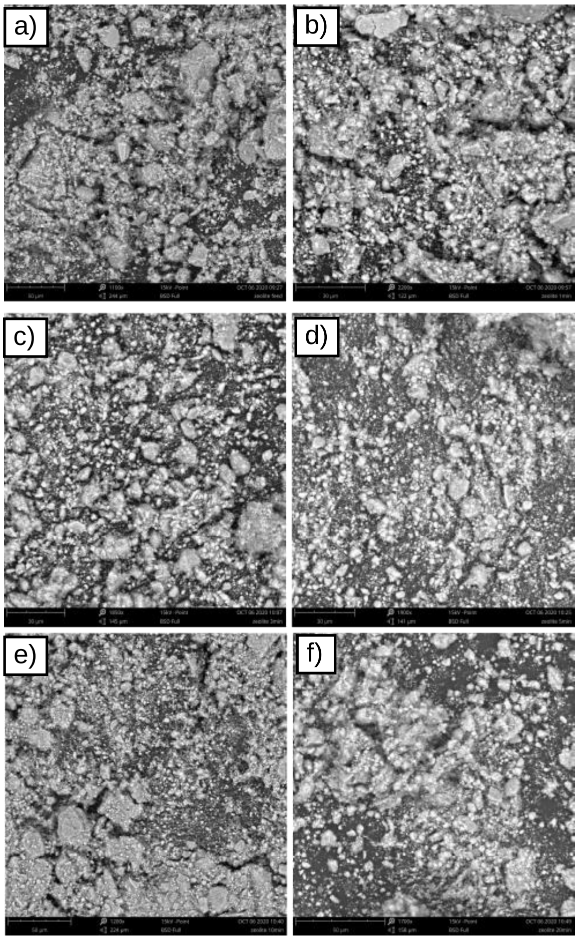

Figure 8

SEM images of the feed and the stirred media mill products.

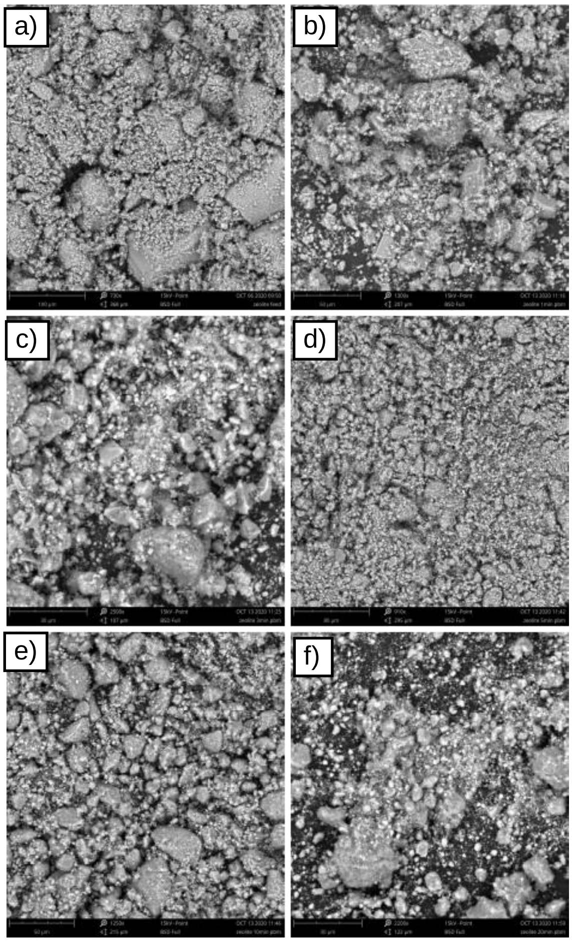

Figure 9

SEM images of the feed and the planetary ball mill products.

angles. On Figure 9, we can find the images for the planetary ball mill products. Here again, we can see the particles becoming smaller and with smoother angles until Figure 9 d), after grinding for 5 min. On Figures 9 e) and f), so the 10 min and 20 min grindings, particles form coarser aggregates. All of this is in good agreement with the previous results.

Conclusion

Our results indicate that the properties of zeolite can be controlled by mechanical activation. Both planetary ball mill and stirred media mill produced particles with significantly finer particle size distribution (with submicron particles) and higher specific surface area compared to the feed material. Grinding kinetics of zeolite was similar but different was observed between efficiency. A first comminution step was noticed, followed by an aggregation step, and then leading to a new, slower, size decrease step. The products of the stirred media mill also had a high specific surface area (SSA) which was demonstrated by the BET measurements. The total SSA of the feed zeolite was 25.17 m^2/g, while the 20 min product had a SSA of 49.09 m^2/g, which is almost twice as high. Such favorable physical properties may lead to a product with high absorption capacity.

When comparing the mechanical activation of zeolite in a dry and horizontal stirred media mill with a dry planetary ball mill, it is clear the highest added value zeolite product was produced with stirred media mill while using much less specific grinding energy than the planetary ball mill.

Further research on this subject could focus on longer grinding times in the stirred media mill.

REFERENCES

1. **Halyag, N., Mucsi, G.:** "Applications of natural zeolite as construction material - Review"Proceedings I. IPW Pécs February 2019, 37–46.
2. **Koshy, N., Singh,D.N.:**"Fly ash zeolites for water treatment applications" Journal of Environmental Chemical Engineering February 2016, 1460–1472.
3. **Zagorskis, A., Baltrėnas, P.:**"Air treatment efficiency of biofilter with adsorbing zeolite layer" Ekologija April2010, 72–78.
4. **Bohács, K., Faitli, J., Bokányi, L., Mucsi, G.:**"Control of Natural Zeolite Properties by Mechanical Activation in Stirred Media Mill" Archives of Metallurgy and Materials June 2017, 1399–1406.
5. **Mucsi, G.:** "A review on mechanical activation and mechanical alloying in stirred media mill" Chemical Engineering Research and Design June 2019, 460–474.