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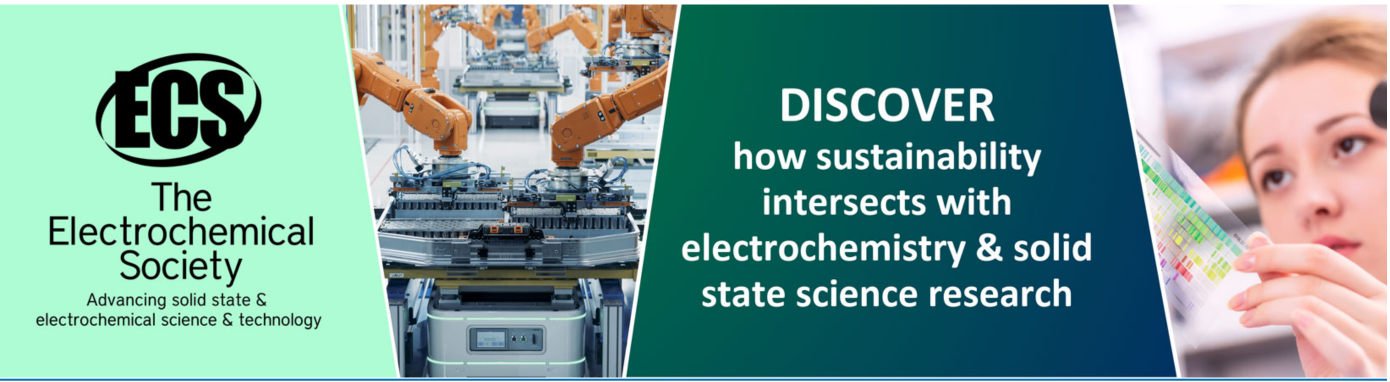

Effect of mechanical treatment on properties of zeolites with chabazite structure

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Abstract. Zeolites are a valuable material having a wide variety of applications. We have examined the effect of mechanical activation on physical-chemical properties of commercial brands zeolite SAPO-34 and SCT-323. It has been shown that the amount of amorphous phase and the specific surface area depends on mechanical treatment. Specific surface area of the zeolites decreases strongly during the grinding process in mills. With the increase of milling time the particles size of zeolites decreased. An increase in amorphisation was observed. Specific surface area of zeolites after mechanical activation in a tumbling ball during 96 hours and annealing up to 800°C with an isothermal holding time of 1 hour does not lead to marked changes and decreases strongly after annealing at 1000°C/h. It has been shown that the milling time of ball milling is a powerful method to obtain the necessary specific surface.

1. Introduction

It is well known that zeolites are crystalline aluminosilicate materials having microporous (zeolite pore) in their structure. They are made of various connections of TO_4 (T = Si or Al) tetrahedral which result in the various zeolite pore sizes and structures [1]. Silicoaluminophosphate molecular sieves (SAPO) are an important class of molecular sieves, which play a unique role in the chemical industry because of their wide applications in catalysis, chemical separation, ion-exchange and membranes [2]. Small-pore SAPO with chabazite (CHA) structure has received great attention in recent years due to its high selectivity to the separation of light gases and methanol to olefin reaction [3].

The specific surface area is a dominant parameter for zeolites [4]. Obtain the necessary magnitude of specific surfaces of materials depends not only on their chemical and mineralogical composition, but also on physical, mechanical and rheological parameters of the used materials [5, 6]. It is known that mechanical processing in activator mills can change the structure, specific surface area, crystal composition of zeolite containing materials and occasionally improve their processing properties [7]. However, the existing published work on mechanical activation of the zeolites is limited. Therefore, the objective of this study was to investigate the effect of mechanical activation and annealing on physical-chemical properties of zeolites SAPO-34 and SCT-323.

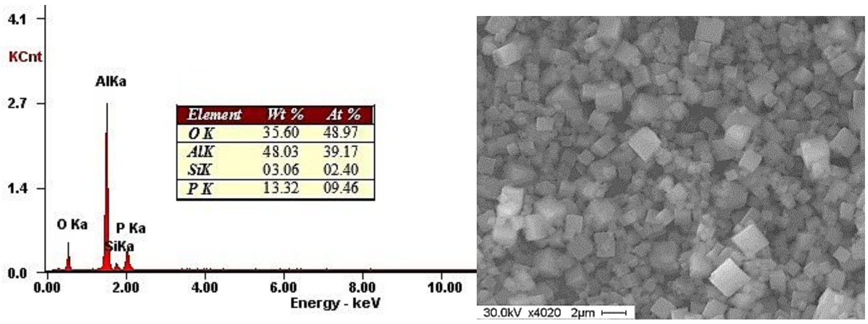
2. Materials and Experimental Procedure

Commercial zeolite powders SAPO-34 and SCT-323 which are chabazite's structural analog from the silicoaluminophosphate group were used as objects of investigation. Mechanical activation of the zeolites was performed in a tumbling mill and a planetary ball mill for 5 minutes and for 100 hours, correspondently. Samples were annealed at temperatures up to 1000°C with an isothermal holding time of 1 hour at each temperatures. The crystal structure and phase composition of the zeolites before and after mechanical activation and annealing were determined by X-ray diffraction analysis (XRD) using diffractometer DRON-3 with Cu-Kα (λ= 1.5418 Å) radiation. The specific surface area of zeolites was determined on an SORBI instrument from low-temperature nitrogen adsorption and on a laboratory-scale apparatus from argon sorption using BET analysis. To study probable changes of morphology powders of zeolite after milling and annealing as well as to confirm the particle size results, all samples were subjected to Scanning Electron Microscopy (SEM).

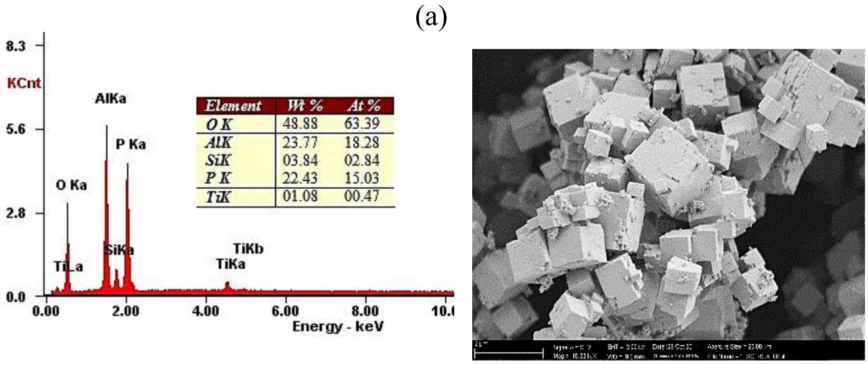
3. Results and Discussion

3.1. Initial powders

Figure 1 and figure 2 represent the elemental analysis, SEM-pictures and X-ray patterns of SAPO-34 and SCT-323.

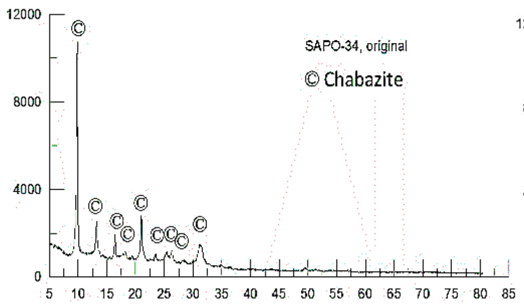


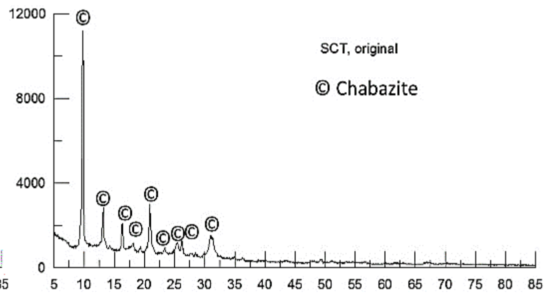
(a)



(b)

Figure 1. Elemental analysis, SEM-picture, for (a) SAPO-34, (b) for SCT-323





(a) (b)

Figure 2. X-ray pattern, for (a) SAPO-34, (b) for SCT-323

The results of elemental analysis showed that the zeolite powders in initial state consisted of Al, O, Si, P for SAPO-34; Zeolite SCT-323 containing titanium and relatively high content phosphorus is different from SAPO-34. The data of SEM showed that particles of zeolite powders are closely matched and have shapes close to cubic with an average particle size 1.5 µm for SAPO-34, 1.7 µm for SCT-323. Calculations of the X-ray patterns showed that the structure of the zeolites consisting Aluminum Silicate Phosphate (PDF-2 00-047-0630). XRD results showed presence of amorphous phase in zeolites, in an amount 83% for SAPO-34, 85% for SCT-323.

3.2. Mechanical activation

This series of zeolites have high specific surface area (561 m^2/g for SAPO-34, 573 m^2/g for SCT-323). Experimental results regarding the change in BET specific surface area of zeolite samples with grinding time in a tumbling ball mill are shown in figure 3. Apparently the specific surface area of the zeolites decreases during the grinding process. In the activation period of the first 12 hours, the specific surface area slightly decreases, and after this period rapidly decreases with prolonging the milling process, so it can be assumed that the minimum values of the specific surface area are achieved after 100 hours of grinding. BET analysis showed that the values of specific surface area of zeolite samples activated for 100 hours were 131 m^2/g for SAPO-34, 103 m^2/g for SCT-323.

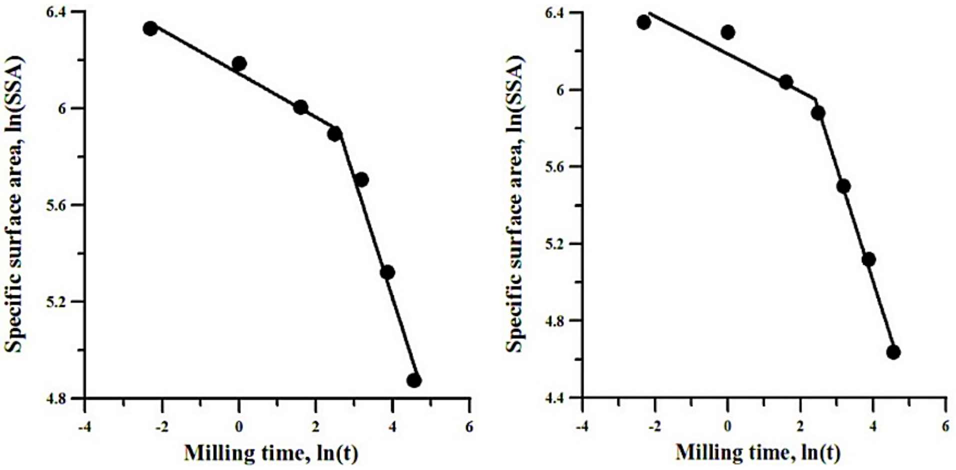


Figure 3. The dependence of specific surface area values of Zeolites from milling times on logarithmic scale, (a) for SAPO-34, (b) SCT-323

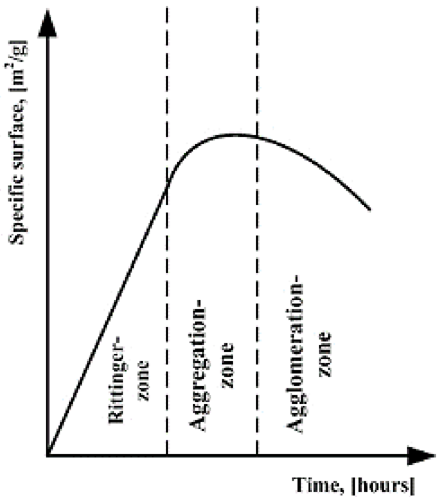


Figure 4. Theoretical curve of specific surface as function of grinding time

The theoretical curve of developed specific surface as function of grinding time is shown in Figure 4. Three well-shaped curves can be observed representing this theoretical curve. They are: Rittinger-zone: the increase of the specific surface is proportional to the grinding time; Aggregation-zone: the intensity with which the increase of the specific surface decreases with the grinding time;

Agglomeration-zone: the specific surface decreases with the comminution time [8, 9]. Because of the small particle size of synthetic zeolite SAPO-34 and SCT-323 with the increase in milling time takes place to agglomeration of particles only. Specific surface area of zeolites correspond to the agglomeration-zone on theoretical curve. Experimental results regarding the change in BET specific surface area of the milled zeolites samples with grinding time in a planetary ball mill are given in Table 1. The decrease in specific surface area is substantial at short grinding times, for instance, surface area reaches about 2.5 times of the initial value after 1 minute milling. BET analysis showed that the values of specific surface area of zeolite samples activated for 5 min were 83 m^2/g for SAPO-34 and 51 m^2/g for SCT-323.

Table 1. Specific surface area, average particle size (d) of zeolites with grinding time in a planetary ball mill

Milling time (min)	Specific surface area (m^2/g)		Grain size in the assumption of sphericity, d (nm)	
	SAPO-34	SCT-323	SAPO-34	SCT-323
0	561.15±13.5	572.99±13	5.3	5.2
1	241±3.61	278±6.93	12	10
3	146.74±2.57	127±2.34	20	23
5	83.63±2.02	51.34±1.61	35	58

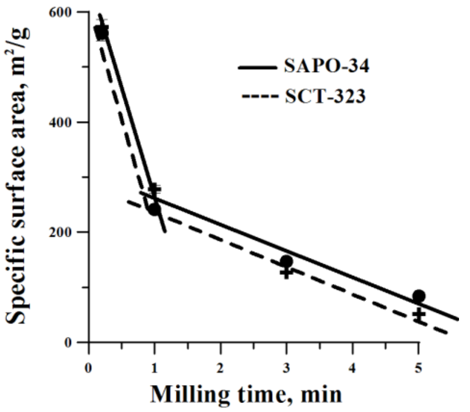


Figure 4. The dependence of specific surface area values of Zeolites from milling times in planetary ball mill

With the increase in milling time, the particles size decreased. The zeolite-average (value in microns) was 1.7 µm for SAPO-34, 1.5 µm for SCT-323. Then, after milling treatment at 24 hours the zeolite-average was 1.5 µm for SAPO-34 and 1.2 µm for SCT-323, after milling treatment at 96 hours the zeolite-average was 0.9 µm for SAPO-34 and 0.7 µm for SCT-323. Moreover most particles have lost their initial cubic shape and converted into spherical and also irregular shapes during the milling process on different milling times.

Selected XRD patterns of mechanically activated zeolite samples are shown in Figure 5. All of the diffraction peaks decreased and/or disappeared with the increase of mechanical activation time. In addition, amorphisation occurred and an increase in amorphisation was observed, from 83 to 90% for SAPO-34 and from 85% to 93% for SCT-323. The tendency of the peaks that belong to the zeolite phase Aluminum Silicate Phosphate to disappear and this tendency increased with the milling time. Koç et al. explained that mechanical activation results in the development of large numbers of dislocations and their associated strain fields, which might lead to an overall decrease in long range lattice periodicity [10].

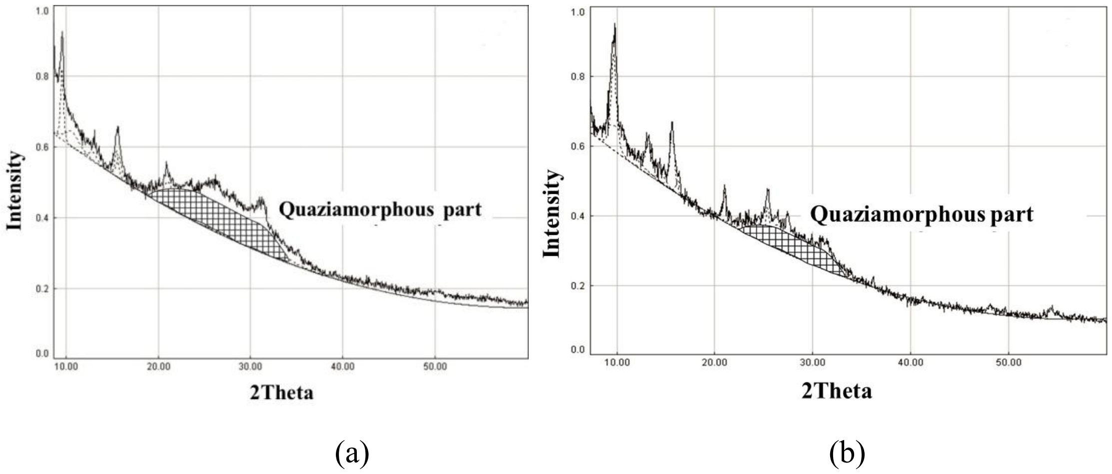


Figure 5. X-ray diffraction patterns of zeolites during 96 hours milling time, for (a) SAPO-34, (b) for SCT-323

The properties of initial zeolites after annealing at 300°C with isothermal holding for 1 hour were studied. The specific surface area was determined at room temperature during a period of 1,000 hours. It has been shown that for the first 24 hours, the specific surface area after annealing was maximum, it decreased for the next 100 hours and after that it remained constant. One can observe the increase of the amount of amorphous phase from 83 to 90% for SAPO-34 and from 85% to 91% for SCT-323, during the 1000 hours period. Specific surface area of zeolites after mechanical activation in a tumbling ball mill during 96 hours and annealing up to 800°C with an isothermal holding time of 1 hour does not lead to marked changes and decreases strongly after annealing at 1000°C/h. Because of the high annealing temperature, sintering particles of zeolites to each other is observed.

4. Conclusion

Milling the particles during a period of 96 hours in a tumbling mill and 5 minutes in a planetary ball mill, the specific surface area is smaller than samples left for lesser periods of time. As for surface morphology, it was observed that the zeolites tended to be spherical in shape; but also irregular in shape after the milling treatment. It has been shown that the milling time of ball milling is a powerful method for obtaining the necessary specific surface due to changing the amount of amorphous phase in the system.

Acknowledgement

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