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Optimized experimental design for natural clinoptilolite zeolite ball milling to produce nano powders

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ABSTRACT

Nano powder of natural clinoptilolite zeolite was mechanically prepared by using a planetary ball mill. Statistical experimental design was applied to optimize wet and dry milling of clinoptilolite zeolite. To determine appropriate milling conditions with respect to the final product crystallinity, particle size and distribution, different milling parameters such as dry and wet milling durations, rotational speed, balls to powder ratio and water to powder ratio (for the wet milling) were investigated. Laser beam scattering technique, scanning electron microscopy and X-ray diffraction analyses were carried out to characterize samples. Results showed that larger than 1 mm particle size of clinoptilolite powder may mechanically be reduced into the size range of less than 100 nm to 30 μm by means of planetary ball milling.

1. Introduction

Zeolites are valuable inorganic materials having wide variety of applications including; molecular sieves, adsorbents, ion-exchangers and catalysts. These materials are microporous crystalline hydrated alumino-silicates composed of TO_4 tetrahedral (T = Si, Al) with O atoms connecting neighboring tetrahedral in which the substitution of silicon by aluminum in framework positions leaves a negative charge behind which in turn may be compensated by some alkali or alkaline earth cations[1–4].

Nowadays, more than 150 different types of zeolites have been synthesized while more than 50 types have been discovered in the nature. Amongst natural zeolites; clinoptilolite, with the simplified ideal formula of $(Na, K)_6Si_{30}Al_6O_{72} \cdot nH_2O$; is one of the most commonly found mainly in sedimentary rocks of volcanic origin. Clinoptilolite-rich tuff is commercially very favorable due to its huge and easy mineable resources as well as, its high zeolite content. This well known zeolite may be utilized for purification and separation processes, removal of NH_4^+ and heavy cations from contaminated water and wastewater, aquaculture, soil fertilizers and conditioners as well as, for dietary supplement in animal nutrition[4–10].

Recently there has been a considerable growing interest in utilizing nanozeolites due to their advantages over conventional micron sized materials. In other words, the reduction of the particle size of zeolites 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. Up to now many different methods for synthesis of nanozeolites have been reported. All of these are based upon hydrothermal treatments which is performed by adjusting effective parameters such as temperature, process duration and ingredient concentrations in order to increase number of durable nuclei and reduce crystal growth [1]. It is reminded, however, that longer synthesis duration, expensive starting materials (specially organic template), lack of reproducibility of the synthesis processes and energy consumption for separation of nano powders by mean of high speed centrifugation are some main issues making the bottom-up chemical synthesis of nanozeolites techno-economically unviable processes [11]. As an alternative technique, the zeolite particle size may be reduced mechanically using specially designed ball mills [12–17]. In previous researches, production of different synthetic zeolites such as Y, X, A, L, ZSM-5 and mordenite was considered utilizing this method [12–17] where possible changes of milled zeolite characteristics when subjected to dry ball milling were well

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Table 1
Variable parameters and their level in designed experiments in this study.

Level	Milling speed (rpm)	Balls to powder ratio in wet milling (wt.%)	Ball to powder ratio in dry milling (No./weight)	Wet Milling period of time (h)	Dry milling period of time (min)	Water to Powder ratio (vol/weight)
1	450	4.5	0.1	2	10	1
2	500	5	0.2	3	20	1.2
3	550	9		4		1.5
4	600					3

investigated. However, results have ascertained that high energy ball milling, decreased the size of aforementioned zeolites. Furthermore, the XRD patterns revealed that the crystallinity of the milled zeolites was also reduced. Thus, collapse of the zeolite crystal structure renders them useless as molecular sieves, adsorbents or shape selective catalysts. In order to overcome this crystallinity problem, wet ball milling of the HY zeolite was investigated. Previous results indicated that by omitting the dry milling step, the crystalline structure of the ground HY zeolite did not collapse completely, even at long milling durations [13]. Furthermore, higher energy efficiencies, lower magnitude of excess enthalpies and elimination of dust formation may also be mentioned as some other added advantages of grinding in aqueous compared to dry medium [13].

In order to evaluate the possibility of production of natural clinoptilolite nano-particles, in this study a combination of wet and dry milling was investigated using a planetary ball mill. To optimize grinding conditions, effective parameters were selected and several sets of experiments were designed based upon statistical methods. Zeolites were milled at different periods of time, milling speed, balls to powder and water to powder ratios. Characteristics of final products such as particle size and distribution as well as, crystallinity of samples were examined by Laser particle size analyzer, scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques.

2. Experimental section

2.1. Ball milling of clinoptilolite zeolite

Powders of natural zeolite (clinoptilolite-rich tuff) were obtained from a mine located in north of Iran near the city of Semnan. Ball milling of clinoptilolite zeolite was performed by mean of a planetary ball mill (PM100; Retsch Corporation). To optimize the milling conditions with respect to size reduction and crystallinity retention, milling parameters such as rotational speed, ball to powder and water to powder ratios as well as, grinding time were varied for different experiments. In most of the performed tests a clinoptilolite powder with particle size of larger than 1 mm was utilized as the starting material in dry milling for a time period of about 10–20 min. The wet milling in water media was then carried out at different periods of time between 2 to 4 h. All of the tests were done in a 250 ml stainless steel jar with protective jacket of zirconium oxide. Zirconium oxide balls of 20 and 3 mm were utilized for dry and wet millings; respectively. The grinding jars were 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 and balls as well as, water in wet milling were placed in the jar at room temperature and atmospheric pressure then sealed and imposed to milling. Due to lack of appropriate accessories to control the temperature and pressure of the jar during grinding , sampling was carried out at the end of this period, at which time the jar was allowed to be cooled down to room temperature. For characterization step the ground powders was dried at 30 °C for 24 h.

2.2. Design of experiments

Different sorts of experiments were designed in order to optimize the appropriate milling conditions for the production of natural clinoptilolite nano-powders with higher crystallinity and lower particle size and distributions. Selected variable parameters and their levels are provided in Table 1. For convenience, the shorthand nomenclature of a, b, c, d, e, f, and g were assigned in which, (a) the dry milling speed, (b) the dry milling time, (c) the ball to powder ratio for dry state, (d) the wet milling speed, (e) the wet milling time, (f) the balls to powders ratio for the wet state and finally (g) the water to powder ratio; were set. Moreover, different conditions for each experiment are presented in this table.

2.3. Characterization

The ground clinoptilolite zeolite was characterized with different instrumental techniques. The morphology of the ground powders as well as its size studied by means of Scanning Electron Microscopy utilizing a LEO 1455vp SEM instrument. XRD patterns to evaluate the crystallinity of the ground powders determined by mean of a STOE STAD-MP Diffractometer in which a copper target at 40 kV and 30 mA (2 h<10_) followed. Furthermore, Particle size measurements of the ground samples performed by laser beam scattering technique through means of a Master sizer 2000 apparatus (MALNERN Instruments).

3. Result and discussion

In order to investigate the effect of different ball milling conditions on size distribution of the ground clinoptilolite zeolite,

Table 2
Different conditions of designed experiments in this research.

No.	code	Dry milling				Wet milling				
		Zeolite powder amount (g)	Ball No.	Rotational speed (rpm)	Duration (min)	Zeolite amount (g)	Balls weight (g)	Rotational speed (rpm)	Water volume (cm^3)	Duration (h)
1	322–3311	50	10	550	20	50	225	550	50	4
2	422–4311	50	10	600	20	50	225	600	50	4
3	322–3313	50	10	550	20	50	225	550	75	4
4	422–3313	50	10	600	20	50	225	550	75	4
5	311–2221	100	10	550	10	100	500	450	100	3
6	000–1322	0	0	0	0	100	500	450	120	4
7	212–1233	50	10	500	10	50	450	450	50	3
8	312–1234	50	10	550	10	50	450	450	150	3
9	311–1213	100	10	550	10	100	450	450	150	3
10	321–2113	100	10	550	20	100	450	500	150	2