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Fabrication of microporous ceramics from ceramic powders of quartz–natural zeolite mixtures

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Abstract

The possibility of producing ceramic powders suitable for the fabrication of microporous filters was investigated through the thermal treatment of the powder mixtures of a high-purity (99.09% SiO_2) quartz and clinoptilolite type of natural zeolite. The quartz and zeolite, mixed in the ratio of 3:1 by weight, was wet ground in a ball mill, the powder was sieved on a 90-μm screen, and the undersize was dried and sintered in the powder form at the temperatures of 1000, 1100 and 1200 °C for 7 h in an air furnace. The powder sinter products were deagglomerated by gentle crushing in an agate mortar and then characterized by phase composition, density, and specific surface area measurements. The added zeolite facilitated the transformation of quartz to cristobalite. The phase transformation of quartz to cristobalite first appeared at around 1000 °C, and, at 1200 °C, led to a ceramic powder sufficiently high in cristobalite content for the fabrication of the microporous ceramic bodies. Re-sintering at 1200 °C of the pressed forms of the ceramic powder resulted in microporous (0.5–3 μm) ceramics with a high porosity of 48.5%, and a three-point bend strength of ~140 kg/cm^2. The ceramics obtained may have potential for filter applications.

Keywords: A. Sintering; A. Powders; B. Porosity

1. Introduction

In addition to a variety of other industrial fields, microporous ceramics have become increasingly popular in manufacturing filters for large-volume solid/liquid separation purposes. Such bulk applications, however, require low-cost mass production of microporous ceramics having desired properties. Ceramic filter media must have high porosity, narrow pore size distribution, and high bend strength as well as high performance in acidic or high-temperature environment, depending upon the intended use. These types of filters have already been fabricated using SiO_2 powders, especially β-cristobalite which is chemically more inert form of SiO_2 and has higher thermal stability and lower density.

Cristobalite can be formed from natural oxides such as crystalline-quartz, flint, and diatomaceous clay. Besides a number of other parameters, the formation of cristobalite phase depends on the sintering temperature and time as well as the properties of the starting materials. Complete phase transformation of well-crystallized pure quartz to cristobalite requires sintering temperatures higher than 1400 °C. However, quartz phase in flint was found to transform completely to cristobalite after heating to 1300 °C for 24 h [1]. The phase transformation temperature lowering effect of flint was attributed to its being rich in crystal defects and grain boundaries that served as nucleation sites. Low-temperature phase transformation of quartz to cristobalite was also observed during heating of diatomaceous clay samples in the temperature range 900–1100 °C, with complete transformation of amorphous diatomaceous silica to crystalline cristobalite within 300 min at 1100 °C [2]. Cristobalite is also likely to form from low-silica zeolites synthesized from china clay by heat treatment at around 1150 °C [3].

Natural zeolites are abundant raw materials in many countries, and have been shown to gain interesting ceramic properties solely through high temperature (~1150 °C) phase transformations [4]. It is also known that ceramic

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powders may be produced from mineral powders through heat treatment in powder form so that they can be subsequently sintered into ceramic forms [5]. In light of these, it is the aim of this investigation to show how it is possible to obtain ceramic powders from the mixture of pure quartz and natural zeolite through heat treatment in powder form so that the ceramic powders can be advantageously used for fabricating microporous ceramic bodies which may have potential for filter applications.

2. Experimental

The starting materials of this study were high-purity quartz (Ezine-Çanakkale-Turkey) and clinoptilolite-type natural zeolite (Manisa-Gördes-Turkey). The compositions of the starting components were analyzed by X-ray fluorescence and listed in Table 1. A laser size analyzer (Malvern) was used for particle size distribution determinations. Micromeritics FlowsorbII-2300 model surface analyzer was used for determining specific surface areas of the powders. Density of the powders was obtained by means of the pycnometer.

The quartz and natural zeolite samples were mixed in the ratio of 3:1 by weight and wet ground in tap water for 80 h, using an alumina ball mill. The ground slurry was dried and sieved on a 90-μm screen. The undersize powder was then sintered in a temperature-controlled air furnace at 1000, 1100 and 1200 °C, without being pressed into any form. The powder sinter products were deagglomerated in an agate mortar with gentle vertical crushing movement for 30 min, and the deagglomerated powder sinters were sieved again on the 90-μm screen. Crystalline phases of all the heat-treated samples and the untreated ground mixture were identified by X-ray diffraction (XRD) analysis.

The 90-μm screen undersize material of 1200 °C sinter powder was formed into a green body by uniaxial pressing at 225 MPa to form rectangular bars measuring 120 mm×50 mm×9 mm. The rectangular bars were re-sintered in the air furnace at 1200 °C. The controlled temperature profile of the furnace during heating and cooling of the raw mixture and the pressed bar samples is given in Fig. 1. The furnace temperature was kept constant for a while, in both the heating and cooling cycles, at the thermal expansion temperature of quartz (α-quartz transforms to β-quartz at the temperature of 573 °C). The constant-temperature sintering time in the furnace was 7 h for all the experiments.

Table 1
The chemical composition, density, sizes and specific surface areas of the raw materials

Chemical composition		
Oxides (%)	Zeolite	Quartz
SiO_2	67.42	99.09
Al_2O_3	14.89	0.14
CaO	2.92	0.02
K_2O	2.34	0.02
MgO	1.20	0.03
Na_2O	0.99	–
Fe_2O_3	0.39	0.03
TiO_2	0.11	0.05
Ignition lost	12.08	0.62
Density	2.32 g/cm^3	2.54 g/cm^3
Specific surface area	41.7 m^2/g	2.5 m^2/g
Size	Finer than 43 μm	Finer than 145 μm

The bar-shaped sinter specimens were characterized by their mechanical strength, apparent porosity, pore size distribution, and the microstructure. Three-point bend strength was measured using Ceramic Instruments Mor-3E model equipment. Apparent porosity was measured by water immersion technique according to Archimedes' principle. Pore size distribution was measured by mercury porosimetry (Micromeritics Autopore II 9220). The microstructure of the bar specimens were investigated by CamScan S4 scanning electron microscope (SEM).

3. Results and discussion

Fig. 2 shows XRD patterns of the ground-and-sieved quartz–zeolite mixtures before and after heat treatment. The mixture with no heat treatment shows mainly two major crystalline phases: α-quartz and clinoptilolite, the major mineral constituent of the natural zeolite. The mixture on heating to 1000 °C indicates a very small quantity of cristobalite formation. The cristobalite peak height increases at higher temperatures, indicating the increasing amounts crystallized. The mixture sintered at 1200 °C can be considered a high-cristobalite silica material, and it may have a potential for use in the ceramic industry because of its expected high thermal stability and acid resistance.

To delineate the influence of mixture powder sintering on improving the formation of cristobalite, the two raw

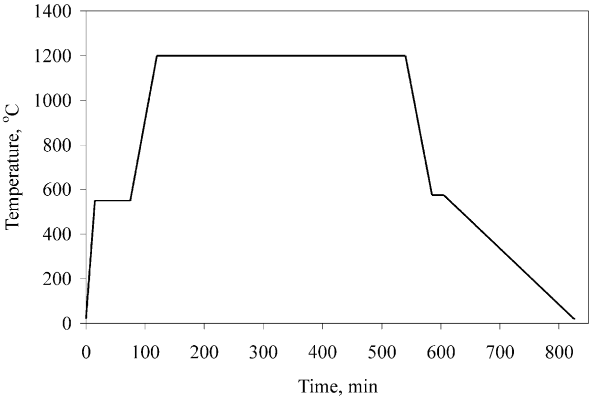

Fig. 1. Heating and cooling profiles of the air furnace for powder and green body sintering.

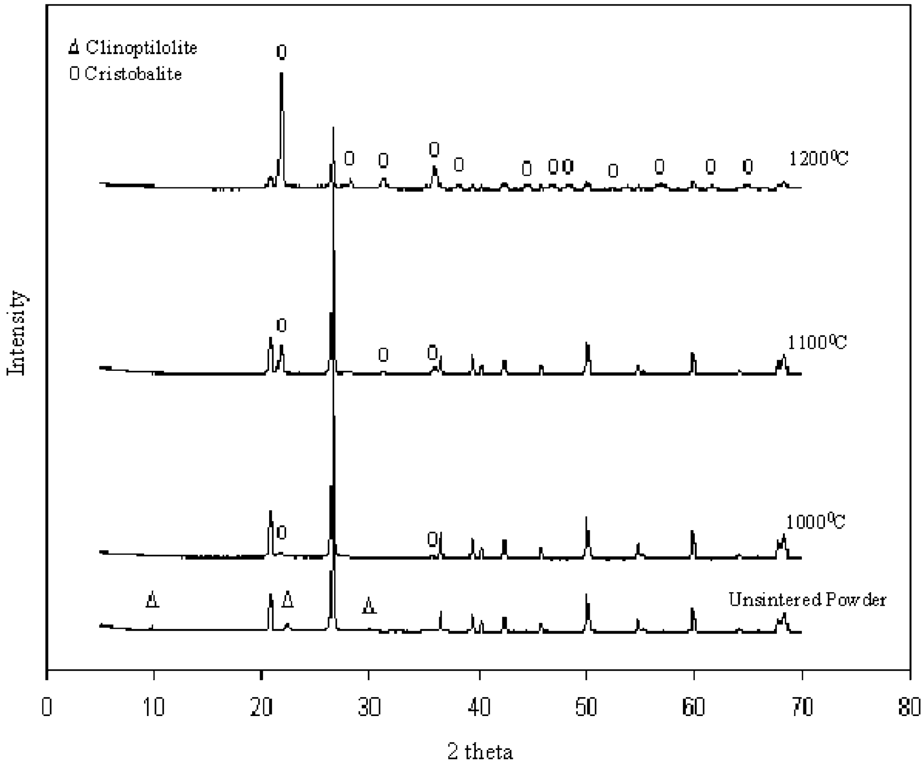

Fig. 2. Phase compositions of the quartz-zeolite mixtures after milling (unsintered) and its powder-sintered forms at 1000, 1100 and 1200 °C.

components of the starting mixture material, the quartz and natural zeolite samples, were wet ground separately, and following the same procedure as described for the powder sintering of the mixtures, the component powders were individually sintered at 1200 °C. Fig. 3 shows powder XRD patterns of the component sinters. Both of the sinter powders indicate very poor formation of β-cristobalite. The zeolite sample was largely converted to an X-ray-amorphous material. It is evident that it is the addition of the right amount of zeolite that promotes the quartz to β-cristobalite transformation. The added zeolite acted as a phase-transforming agent; it melted at a lower temperature (around 800 °C), and further heating provided good dispersion of the liquid phase through the quartz particles, leading to an increased crystallization of SiO_2 to β-cristobalite.

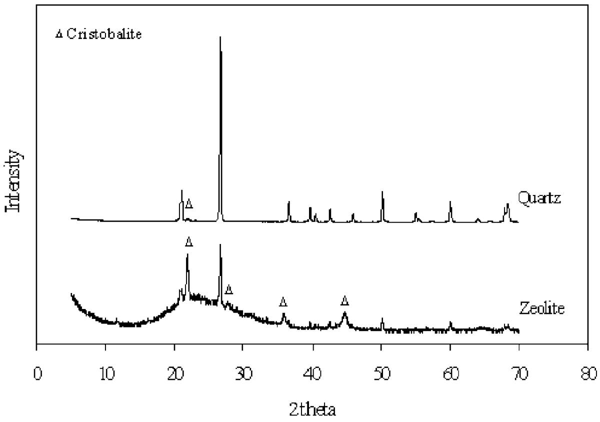

Fig. 3. Phase compositions of the quartz and zeolite powders after singly sintered at 1200 °C.

Fig. 4 shows size distributions of the mortar-deagglomerated sinter particulates of the heat-treated mixtures, and also the size distribution of the ground and sieved mixture without heat treatment. A comparison of the size distribution curves of the heat-treated samples reveals that the proportions of the finer size fractions of the 1200 °C sample are considerably higher than the 1000 and 1100 °C samples. This is again an indication of the higher amount of brittle crystalline phase (β-cristobalite) in the 1200 °C sample.

Table 2 shows specific surface area and density of the mortar-deagglomerated sinter particulates of the low- (800 °C) and high-temperature (1000, 1100, 1200 °C) powder sinters of the mixtures. The high specific surface

Table 2
The specific surface area and density of sintered powders at low and high temperatures

	Powder sintering temperature (°C)			
	800	1000	1100	1200
Specific surface area (m^2/g)	8.64	1.17	1.22	0.44
Density (g/cm^3)	2.56	2.50	2.42	2.27

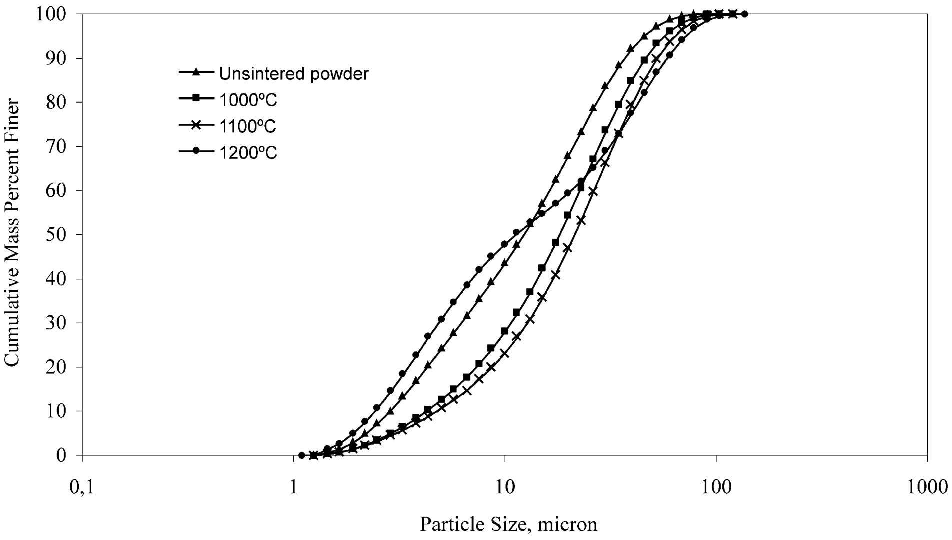

Fig. 4. Size distributions of unsintered and mortar-deagglomerated sinter powders.

area of the 800 °C sample suggested that the zeolite in the mixture did not undergo much structural change at that temperature. The specific surface area and density of the deagglomerated sinters were appreciably lower for the samples of high-temperature treatments. The change in the density can be mostly attributed to the phase transformation of SiO_2 to cristobalite, normally having lower density than quartz. The lowering of the specific surface area is an indication of the success of sintering in the powder form. High silica in the mixture must have prevented the local, massive vitrification of the zeolite particles during sintering. A good sintering also requires effective spreading of the melted zeolite through the loosely deposited quartz particles by wetting the surfaces. The cristobalite is likely to form first at the interface between the melted material and the silica particle [6], and the crystallization increases upon further heating.

The low specific surface area of the 1200 °C sinter powder should be favorable in using this material for producing permeable microporous ceramic bodies. For this purpose, the sinter powder was shaped into rectangular bars by unixally pressing at 225 MPa, and the green body was sintered at 1200 °C. The properties of the ceramic bodies produced as such were compared with those of the sintered ceramic bodies produced from the same starting materials through the same processing steps, but without pre-sintering of the mixture in powder form. Table 3 gives a comparison of the properties of the ceramic bodies formed with and without pre-sintering. The use of pre-sintered mixture powders enabled the fabrication of microporous (0.5–3.0 μm) ceramic bodies with higher porosity and strength. The SEM micrographs of the ceramic bodies (Figs. 5 and 6) reveal the better microstructural features of the ceramic body produced from the pre-sintered powder, having a homogenous pore distribution and no local, massive vitrification of zeolite. Without pre-sintering, quartz particles are embedded in massive, vitrified

Table 3
Properties of ceramic bodies produced from mixture powders with and without pre-sintering in the powder form (pre- and post-sintering temperatures: 1200 °C)

	Density (g/cm^3)	Porosity (%)	Bend strength (kg/cm^2)	Pore size range (μm)
Form sintering of pre-sintered powders	2.17	48.5	142.4	0.5–3.0 (median: 1.37)
Form sintering without pre-sintering	2.24	38.3	135.7	not measured

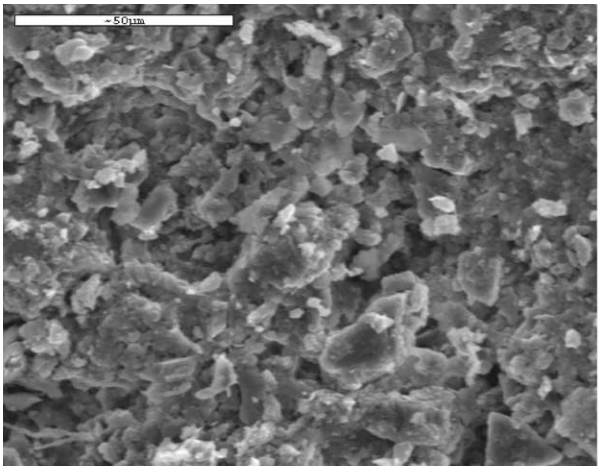

Fig. 5. SEM micrograph of a typical fracture edge of the ceramic body formed from a pre-sintered powder.

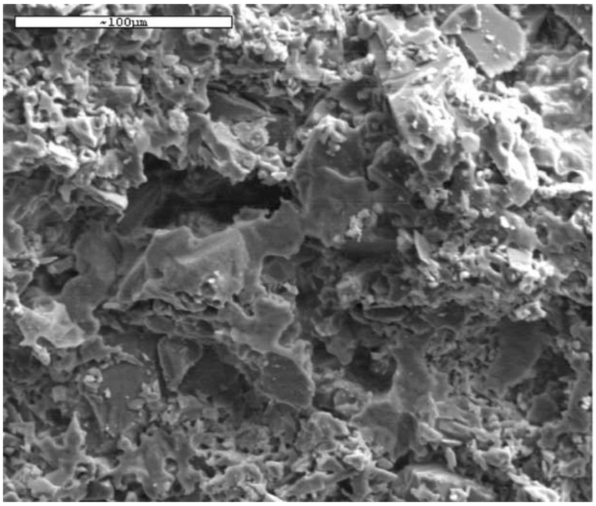

Fig. 6. SEM micrograph of a typical fracture edge of the ceramic body formed from an unsintered starting powder.

zeolite phases, rather than a surface wetting of the quartz particles by zeolite.

4. Conclusion

Powder sintering of a high-purity quartz at 1200 °C by the addition (25 wt.%) of clinoptilolite type of natural zeolite enabled the production of a high-cristobalite silica material from which high-porosity (48.5%), microporous (0.5–3.0 µm) ceramic bodies with sufficiently high strength (142.4 kg/cm^2) can be fabricated by press forming and sintering. Such ceramic bodies may have potential for use in a variety of fields as filtering media and/or support. The success can be explained by the pre-sintering of mixtures in the powder form, as the sintering of the natural zeolite and the quartz powders alone at the same temperature produced much less crystallization of cristobalite.

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