

Nanocrystalline Macroporous Wollastonite Ceramics – A Spectroscopic View

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Abstract

Nanocrystalline macroporous CaSiO₃ ceramic powders have been synthesized by a novel low temperature initiated self-propagating, gas producing solution combustion process. The effects of temperature on crystalline phase formation, amount of porogens and particle size of porous CaSiO₃ have been investigated. Single phase β -CaSiO₃ and α -CaSiO₃ are formed at much lower temperatures to the powders obtained via solid state reaction method. On calcination the samples becoming more porous and the pore diameter increases from 2 to 8 μm . The samples calcined at 950 °C has 17.5 % porosity, and the porosity increases to 31.6 % at 1200 °C. The surface area of as formed and calcined at 950 and 1200 °C of CaSiO₃ samples were found to be 31.93 m²/g, 0.585 m²/g and 3.48 m²/g respectively. The TL intensity in powdered sample is more when compared to the pelletized CaSiO₃ and it is further observed that there is a shift in glow peak temperatures in pelletized sample. This is attributed to the inter particle spacing and pressure-induced defects. The structure of CaSiO₃ has been investigated by ²⁹Si MAS NMR..

INTRODUCTION

In recent years, materials with porous architecture and high surface area are being developed for numerous potential applications in nanotechnology. Since the discovery of the ordered mesoporous silica [1], a lot of porous materials have been synthesized using surfactants as template. However, most of these materials are unstable on removal of the surfactant and the porous skeleton collapse easily when heated above 400 °C. Therefore, new methods of synthesis which give higher stability are desirable.

In the present study, we describe a simple and quick method of preparing nanocrystalline macroporous wollastonite (CaSiO₃) ceramic powders. The main advantage of this method is the ability of maintaining porous structure even at elevated temperatures and moreover, the pore diameter increases upon heating. High thermal stability of porous materials can combine porous structure with traditional ceramic science and technology, leading to wide applications.

EXPERIMENTAL

The stoichiometry of the redox mixture used for combustion process was calculated using the total oxidizing and reducing valencies of the ingredients, following the concept used in propellant chemistry. The fuel diformyl hydrazine (C₂H₄N₂O₂, DFH), used for combustion synthesis, was prepared in our laboratory by the reaction of formic acid and hydrazine hydrate as described in the literature [2]. For the preparation of wollastonite, the required mole ratio of Ca(NO₃)₂·4H₂O:SiO₂:DFH was 1:1:1.25. The samples have been studied by various spectroscopic techniques like XRD, TG/DTA, EDS, SEM, FTIR, Thermo

luminescence (TL) and MASNMR. The powder (1mg) as well as the pellets (before and after heat treated) are irradiated with gamma rays (Co⁶⁰ source) for a dose of 1 - 5 KGy for TL studies.

RESULTS AND DISCUSSION

The phase evaluation of the as formed and calcined powders of CaSiO₃ was examined by powder X-ray diffraction and is shown in Fig. 1. It has been observed that the peaks of CaSiO₃ become more and more intense with increase in calcination temperatures from 500-950 °C. On further increase in calcination temperature from 950 - 1200 °C, the simultaneous existence of CaSiO₃ in β and α phases could be observed at 1100 °C. Single phases of β -CaSiO₃ and α -CaSiO₃ can be synthesized at 950 and 1200 °C, respectively. The phase transformation temperatures of combustion derived wollastonite powders were found to be lower to the powders obtained via solid-state reaction method. It was observed that the average particle size of the annealed CaSiO₃ samples is in the range 29–50 nm. The nominal composition of the ceramic powders was confirmed by EDS.

The size morphology and distribution of the (a) as formed and calcined at (b) 950 °C and (c)1200 °C CaSiO₃ powders was examined using a SEM and are shown in Fig. 2. It is interesting to note that, with increase of temperature the samples becoming more porous and the pore diameter increases from 2 – 8 μm . The as formed sample shows uniform distribution of nanosized particles. The calculated porosity values are 17.5 % and 31.6 % at 950 °C and 1200 °C respectively. The surface area of as formed CaSiO₃ and calcined at 950 and 1200 °C are 31.93, 0.585 and 3.48 m²/g respectively

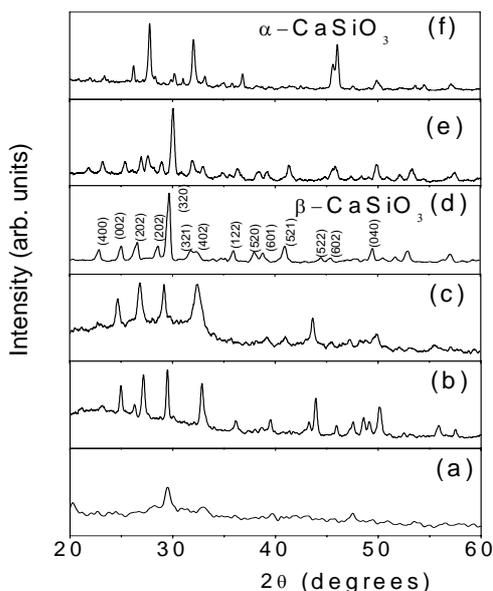


Fig. 1. PXRD patterns of combustion derived CaSiO_3 powders (a) as formed (b) 500 °C (c) 700 °C (d) 950 °C (e) 1100 °C and (f) 1200 °C.

The large surface area ($31.93 \text{ m}^2/\text{g}$) of as made sample is due to uniform distribution of nano sized particles. On heating the sample at 950 °C, the surface area decreases to $0.585 \text{ m}^2/\text{g}$ might be due to the growth in particle size or agglomeration. On further calcination to 1200 °C the surface area increased to $3.48 \text{ m}^2/\text{g}$ is due to the swelling of agglomerated powder particles.

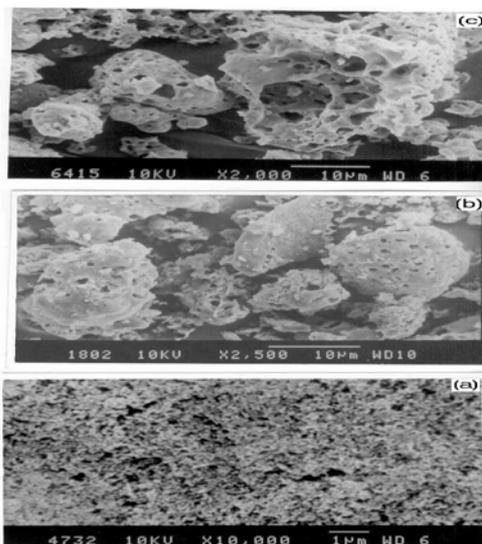


Fig. 2. The SEM images of combustion derived wollastonite powders (a) as formed (b) calcined at 950 °C (c) calcined at 1200 °C.

The TG curve shows about 9% weight loss around 120 °C, which can be attributed to the vaporization of hydrated and coordinated water molecules. From TG

curve it is also observed that further weight loss takes place at two stages, one around 530 °C with endothermic peak corresponding to 25% of total weight loss and another one at 745 °C corresponding to total 33% weight loss. Besides to TG-DTA evidence, the IR spectra of the as formed and calcined samples at different temperatures also witnessed the presence of water molecules. This weight loss should be either the release of trapped and very strongly bonded water molecules or correspond to OH groups, in agreement with the ^{29}Si MAS NMR experiments (Fig. 3) showing the transformation of Q_1 and Q_2 into Q_3 . The exothermic peak at 890 C in the DTA curve indicates starting of crystallization of CaSiO_3 and a phase transformation into β -wollastonite in confirmation with XRD results.

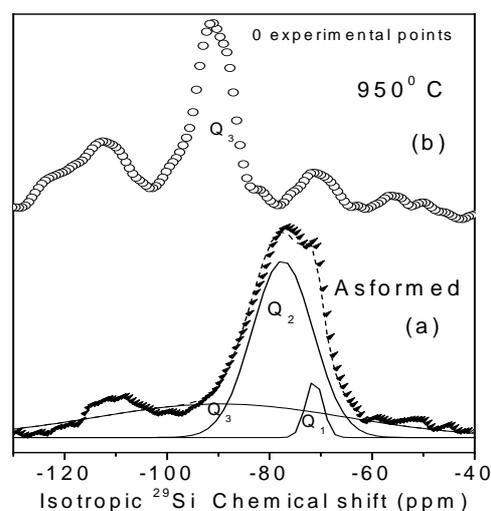


Fig. 3. ^{29}Si MAS NMR spectrum of CaSiO_3 (a) as formed* (b) calcined at 950 °C* Deconvoluted Gaussian line shapes for each Q^n obtained from a least-square analysis. MAS spectrum is shown in open circles and the dashed line is the theoretical fit.

The ^{29}Si MAS NMR exhibits the resonances at -71.29 , -77.45 and -89.52 ppm and are assigned to Q_1 , Q_2 and Q_3 units, respectively. For fully crystalline sample of CaSiO_3 (950 °C 3 h), shows only one fairly narrow peak centered at -90.31 ppm indicating a largest amount of silicon in the sample present as Q_3 groups. The TL intensity is more in powdered sample compared to pelletized sample. This might be attributed to the physical nature, structure of the sample. The shifts in TL glow peaks as well as reduction in TL intensity in pelletized samples are attributed to inter particle spacing and pressure induced defects.

REFERENCES

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2. C. Ainsworth, R. Jones, J. Am. Chem. Soc. **77** (1995) 621.