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Thermally activated sintering–coarsening–coalescence-polymerization of amorphous silica nanoparticles

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Abstract

An onset sintering–coarsening–coalescence-polymerization (SCCP) event of amorphous SiO_2 nanoparticles (ca. 40–100 nm in size) by isothermal firing in the 1150–1300 °C range in air was characterized by an N_2 adsorption–desorption hysteresis isotherm coupled with X-ray diffraction and vibrational spectroscopy. The apparent activation energy of such a rapid SCCP process was estimated as 177 ± 32 kJ/mol, based on 30% reduction of a specific surface area with an accompanied change of medium range orders, i.e. forming Si_2O_5 while retaining the Si–2ndO yet losing the Si–2ndSi without appreciable crystallization. The minimum temperature of the SCCP process, as of concern to industrial silica applications and sedimentary/metamorphosed sandstone formation, is 1120 °C based on the extrapolation of steady specific surface area reduction rates to null.

Keywords: Amorphous SiO_2; Coalescence; Coarsening; Early stage sintering

1. Introduction

Nanocrystalline powder compacts were known to reduce total surface area by the thermally activated processes of sintering, coarsening and coalescence [1–4]. Such processes occur readily for nanocrystals having relatively high specific surface area and high homologous temperature (T/T_m, where T_m is the melting point in Kelvin) given a lowered melting point [5] against the firing temperature. This has been experimentally proven for ionic oxide nanoparticles, such as equi-axed γ-Al_2O_3 [1], platy cobalt oxide [2], hexagonal rods of ZnO [3], and equi-axed ZrO_2 vs. the less refractory TiO_2 [4], based on electron microscopic observations coupled with BET/BJH measurements of specific surface area and pore size/shape changes of dry pressed samples subjected to isothermal firing at temperatures for minutes (BET and BJH denote the Brunauer–Emmett–Teller method [6] and Barrett–Joyner–Halenda method [7], respectively).

The specific-surface-area change rate in the steady state was used to determine the apparent activation energy of a vigorous onset sintering–coarsening–coalescence event for the above crystalline oxide nanoparticles [1–4]. A surprisingly low apparent activation energy for the ZrO_2 nanoparticles in comparison with that for less refractory and small-sized γ-Al_2O_3 nanoparticles was attributed to extensive polymorphic transformations of ZrO_2 for enhanced plasticity [4]. In addition, the minimum temperature for such processes to occur was estimated to be 516, 641 and 710 °C for nanosized ZnO [3], TiO_2 and ZrO_2 [4], respectively, based on the extrapolation of steady specific-surface-area reduction rates to null.

Here the BET/BJH method is further employed to study the onset sintering–coarsening–coalescence-polymerization (SCCP) of amorphous SiO_2 nanoparticles which have only 50% ionicity [8] and hence 40% higher bond strength (106 kcal/g-atom) than ionic oxides [9]. We focused on the activation energy and minimum temperature for incipient SCCP of the amorphous SiO_2 nanoparticles and the underlying effect, if any, of their structure change in terms of medium range order (MRO). This subject is of concern not only for the rapid assembly of SiO_2 nanocondensates by pulsed laser ablation (PLA) under the influence of radiant heating [10], but also for a number of industrial

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applications [11–14] and natural occurrences at high temperatures [15].

2. Experimental

The starting amorphous SiO_2 nanoparticles (UR ISIL001 99.8%) prepared by a sol–gel synthesis route were characterized by transmission electron microscopy (JEOL3010 at 200 kV) coupled with energy-dispersive X-ray analysis to be spherical, 40–100 nm in diameter and free of impurities (Appendix A). A fixed amount (0.06 g) of such SiO_2 nanoparticles was mixed with 1 wt% poly-vinyl alcohol (PVA) and then dry-pressed at 650 MPa into disks ca. 5 mm in diameter and 2 mm in thickness followed by isothermal firing at 1150–1300 °C for up to 60 min in air. The disks were fired in 10 min increments at 1150 °C but shorter increments (5, 3 or 1 min) at 1200, 1250 and 1300 °C in air until more than 70% reduction of the specific surface area was noted.

Microstructures of the dry-pressed and heat treated samples were studied by scanning electron microscopy (SEM, JEOL 6330 at 10 kV). The phase identity of each sample was determined by X-ray diffraction (XRD, CuKα; 40 kV, 30 mA at 0.05° and 3 s per step) in the 2θ range of 5°–50° and Raman spectra using laser excitation (633 nm) having a spatial resolution of 1 μm (HORIBA HR800). The pulverized samples were also mixed with KBr for Fourier transform infrared spectroscopy (FTIR, Bruker 66v/S, 64 scans in the range of ~400–4000 cm^{-1} with 4 cm^{-1} resolution) study of OH^- signature and structure unit changes of representative samples.

Nitrogen adsorption/desorption isotherms of the dry-pressed and then heated powders were conducted at a liquid nitrogen temperature of 77 K using a Micromeritics ASAP 2020 instrument. The surface area and pore size distributions were obtained from the N_2 adsorption and desorption branch, using the BET [6] and BJH method [7], in low and high relative pressure (P/P_o) range, respectively where P_o is the saturation pressure determined as ~760–762 mmHg. A filler rod containing the SiO_2 sample was pumped down to 10^{-3} Torr for degassing at 300°C followed by BET/BJH measurements at a relative pressure increment 0.05. The BET isotherm and BJH adsorption/desorption hysteresis type of the samples are classified according to the scheme of International Union of Pure and Applied Chemistry [16]. The H1 type adsorption/desorption hysteresis loop of the type IV isotherm (cf. Appendix A of Ref. [1]) was used as an indicator of cylindrical pore occurrence.

3. Results

3.1. BET/BJH observations of pore and specific surface area changes by firing

BET data of the fired samples indicated that the specific surface area decreases with an increase in dwelling time at a specific firing temperature for SiO_2 powders as compiled

Table 1
BET/BJH data and phase identity of 40–100 nm-sized amorphous SiO_2 powder subjected to various heating treatments.

T (°C)–t (min)	Specific surface area (m^2/g)	Ads./desorp. pore width (nm)	Phases
Dry-pressed	43.72	22.4/20.0	amp 1
1150–10	37.46	20.8/17.7	amp 2
1150–20	31.11	26.2/22.1	amp 2
1150–30	30.42	22.4/20.5	amp 2
1150–40	22.35	29.2/22.8	amp 2
1150–50	16.68	27.4/22.2	amp 2
1150–60	10.23	21.3/14.0	amp 2
1200–5	41.07	20.4/18.6	amp 2
1200–10	24.34	25.6/21.8	amp 2
1200–20	14.15	28.2/19.5	amp 2
1200–30	10.63	38.5/20.6	amp 2
1250–3	40.58	22.8/20.1	amp 2
1250–5	39.65	22.8/20.7	amp 2
1250–7	33.23	25.6/22.6	amp 2
1250–8	27.04	23.3/20.4	amp 2
1250–9	24.4	22.3/19.9	amp 2
1250–10	14.22	25.5/18.1	amp 2
1250–20	2.94	12.1/7.9	amp 2
1300–3	37.80	20.8/18.5	amp 2
1300–5	37.14	24.1/20.4	amp 2
1300–7	17.51	36.0/22.6	amp 2
1300–10	10.74	29.5/17.3	amp 2

Note: The abbreviation ads./desorp. denotes adsorption/desorption and the amorphous (amp) phases 1 and 2 have double (peaks at ca. 13° and 22°) and single (peak at ca. 22°) broad diffractions according to XRD. The crystalline silica phases, i.e. tridymite and cristobalite did not occur unless heated for a prolonged time, e.g. beyond 40 min at 1300 °C in the presence of PVA (Fig. 3).