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Self-organized formation of spherical porous granules only by one-step heat-treatment in MgO-Fe₂O₃-Nb₂O₅ system

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Abstract

In this letter, a new process to obtain spherical porous granules (SPGs) is presented, namely self-organized formation only by a one-step heat-treatment. Commercial MgCO₃ (basic), α -Fe₂O₃ and Nb₂O₅ powders of Mg:Fe:Nb = 1:1:1 in mole fraction were wet-ball milled, and were heat-treated in air at 800-1350°C. The samples heated at $\geq 1100^\circ\text{C}$, most of the samples became SPGs with the diameter of ~ 50 -100 μm , containing 3-D network structure. The main constituent phase of porous spheres was pseudobrookite-type MgFeNbO₅. The formation mechanism of porous microspheres was discussed by using SEM observation and high-temperature XRD analysis.

Keywords: porous spheres, granular materials, self-organization, pseudobrookite, MgFeNbO₅

1. Introduction

Porous ceramics are widely used for fluid filters, catalysts, catalyst supports, lightweight structural materials, and so on. Among various shapes of the porous ceramics, spherical porous granules (SPGs) are favorable for heterogeneous catalysts, photonic materials, chromatography supports, drug delivery carriers, and healing of defective bones [1-4]. A variety of processes, mostly liquid-based, have been developed to synthesize SPGs [1, 5-15]. To synthesize SPGs, solid-based processes have seldom been realized, except the mechanical granulation method with rotating fluidized bed [16].

We developed uniformly porous ceramics with 3-D network structure (UPC-3D) by using pyrolytic reactive sintering of powder mixtures including gaseous species such as carbonates and hydroxides [17,18]. Stimulated by Bayer's [19] early report in 1971 on pseudobrookite-type ceramics (generally expressed as Me₃O₅), uniformly porous MgTi₂O₅ [20-21], and its derivative, bulk MgFeNbO₅ (Fe³⁺ + Nb⁵⁺ substitute 2 Ti⁴⁺) have recently been synthesized [22]. In this previous report on bulk MgFeNbO₅ [22], mold-pressed compacts of mortar-mixed powders of MgCO₃ (basic), α -Fe₂O₃ and Nb₂O₅ were sintered in air to obtain relatively dense materials. However, when the ball-milled powder mixture was simply heated in air, we have found the self-organized formation of

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SPGs, mainly composed of MgFeNbO_5 phase. Here we present the new process to synthesize SPGs only by one-step heat-treatment in the $\text{MgO-Fe}_2\text{O}_3\text{-Nb}_2\text{O}_5$ system.

2. Experimental

MgCO_3 (basic) ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, 99.9%, Kojundo Chemical Laboratory), $\alpha\text{-Fe}_2\text{O}_3$ and Nb_2O_5 (99.9% each, Wako Pure Chemical Ind.) powders were used as the starting materials, similar to the previous report [22]. The MgCO_3 (basic), $\alpha\text{-Fe}_2\text{O}_3$ and Nb_2O_5 powders ($\text{Mg:Fe:Nb} = 1:1:1$ in mole fraction) were wet-ball milled for 24 h in ethanol with ZrO_2 balls, dried and sieved through 100 mesh screen ($<150 \mu\text{m}$). The mixed powder was heated at the ramp rate of $10^\circ\text{C}/\text{min}$, up to the maximum temperatures from 800 to 1350°C , and then cooled to room temperature without holding time. For the precise temperature control, TG-DTA apparatus is useful, but normal air furnaces can also be used.

The microstructure of the heat-treated products was characterized by scanning electron microscopy (SEM, SU-70, Hitachi High-Tech.) and digital optical microscopy (VHX-1000, Keyence Co.). The reaction behavior of the MgCO_3 (basic)- $\text{Fe}_2\text{O}_3\text{-Nb}_2\text{O}_5$ mixed powder (without compressing) was analyzed by high-temperature X-ray diffraction (HT-XRD, Multiflex, $\text{Cu-K}\alpha$, 40 kV and 40 mA, XRD, Rigaku), from room temperature to 1350°C in air. Diffraction patterns were acquired at 100°C each up to 1000°C , and 50°C each up to 1350°C . The ramp rate of the furnace was $10^\circ\text{C}/\text{min}$. XRD patterns were acquired after 5 min holding at each temperature. The scanning rate was $2\theta=4^\circ/\text{min}$ and the scanning range was $2\theta=10\text{-}60^\circ$, hence, 5 min holding + 15 min scanning at each temperature.

3. Results and discussion

Fig. 1 shows representative SEM images of (a) the MgCO_3 (basic)- $\alpha\text{-Fe}_2\text{O}_3\text{-Nb}_2\text{O}_5$ mixed powder and (b) its heat-treated-only product (SPGs) at 1350°C (ramp speed: $10^\circ\text{C}/\text{min}$, holding time: 0 min), and (c) a digital optical microscope image (real color) of SPGs. The microstructure was drastically changed only by the simple heating. In order to verify the microstructure development during the heating, Fig. 2 shows lower magnification SEM images of the heat-treated products at $800\text{-}1300^\circ\text{C}$. To prepare the SEM samples, heat-treated products were spread on a carbon tape using a spatula, and coated with Pt by sputtering. At 800°C , the surface of fine particles reflected the sample preparation with a spatula (i.e., like spread butter with a butter knife), but special structural feature was not observed. At 900°C , a part of fine particles started to form SPGs with the diameter of $\sim 50 \mu\text{m}$. At 1000°C , formation of SPGs became frequent. The spherical granules seem to be soft due to the weak bonding among primary particles, because the surface of some granules was slightly flattened by the sample preparation. At $>1100^\circ\text{C}$, most of the sample became SPGs, with typical diameter of $\sim 50\text{-}100 \mu\text{m}$.

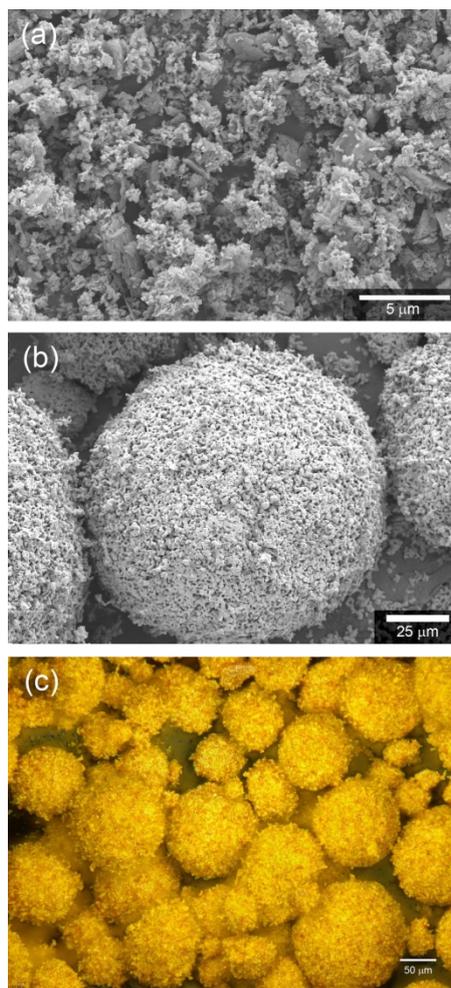


Fig. 1

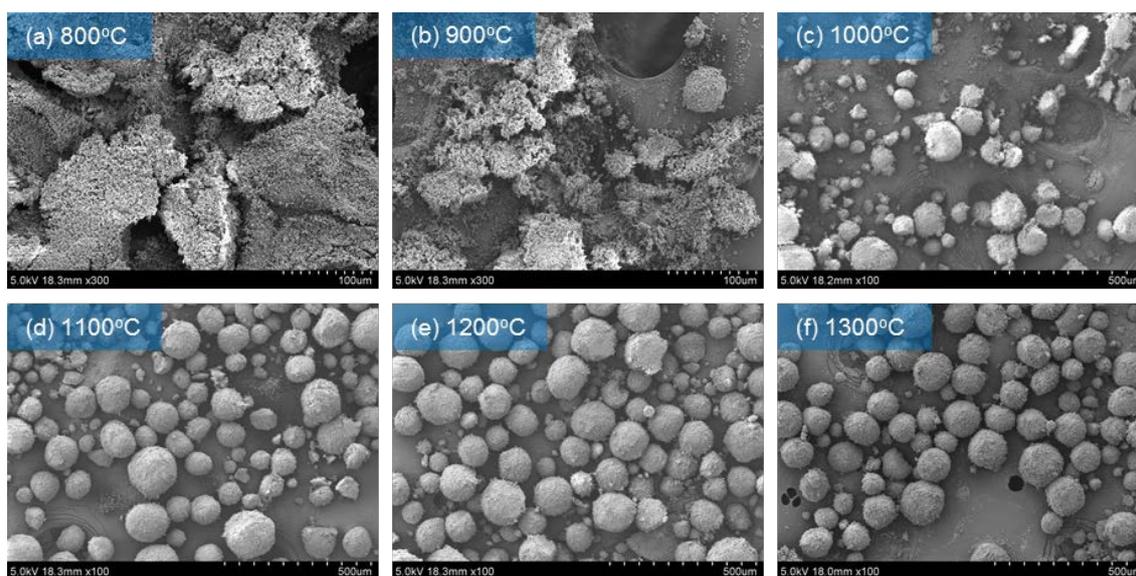


Fig. 2

Figure 3 shows higher magnification SEM images of the heat-treated products from the MgCO_3 (basic)- α - Fe_2O_3 - Nb_2O_5 mixed powder. At 800°C , the microstructure was similar to that of the as-mixed powder at room temperature (Fig. 1(a)), however, at 900°C , the primary particles start to connect to each other. Somewhat large and rod-like grains observed at 800 - 1000°C are attributed to the pseudomorphs (remnants of original shape) consisted of fine MgO particles from hydromagnesite. At $\geq 1100^\circ\text{C}$, curved and so-called "L-shaped" grains were observed, which are typically found in pseudobrookite-type ceramics with some liquid phase [20-22], and necking between particles became firmer. At 1300°C , although some grains with intermediate clombite-type and spinel-type structures remained at the surface, most of the product converted into pseudobrookite-type MgFeNbO_5 .

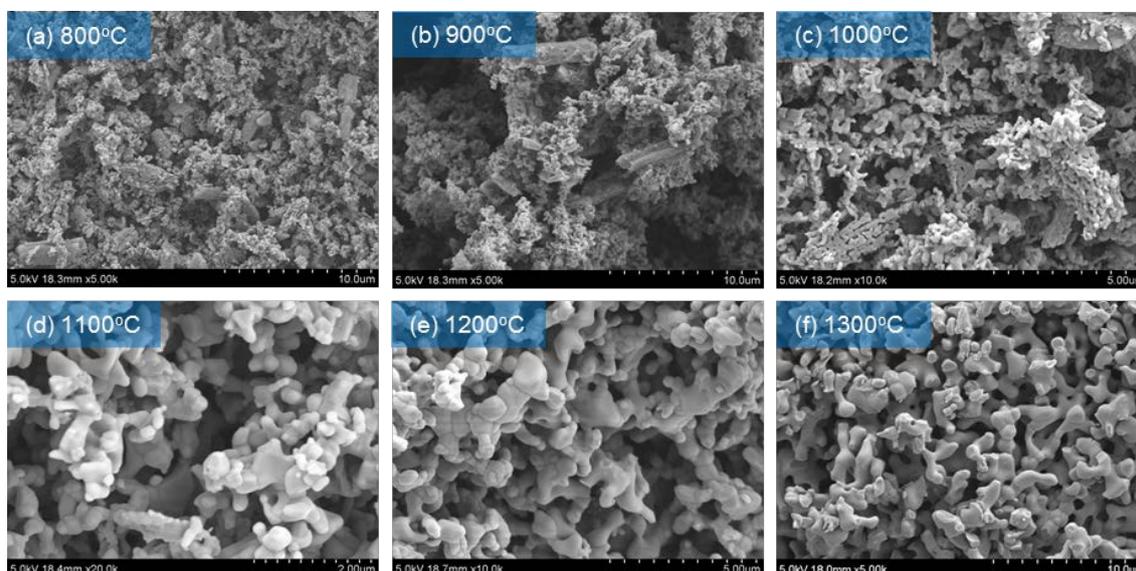


Fig. 3

The reaction behavior of the MgCO_3 (basic)- α - Fe_2O_3 - Nb_2O_5 mixed powder during the heat-treatment was analyzed by HT-XRD as shown in Fig. 4. All peaks before heating were well-indexed with $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (hydromagnesite, ICDD PDF #25-0523), α - Fe_2O_3 (hematite, #33-0664), and low-temperature phase Nb_2O_5 (#27-1003). The thermal decomposition of hydromagnesite completed at $\sim 500^\circ\text{C}$ (confirmed by TG-DTA, Fig S1), and MgO nanocrystals was formed from hydromagnesite as shown in Fig. 4. As shown in Fig. 3, MgO nanocrystals kept the pseudomorphs of hydromagnesite at intermediate temperatures (~ 500 - 800°C). At ~ 900 - 1000°C , the formation of intermediate clombite-type MgNb_2O_6 (ss) and spinel-type MgFe_2O_4 (ss) phases started. At $\sim 1100^\circ\text{C}$, the formation of pseudobrookite-type MgFeNbO_5 started. At 1300°C , pseudobrookite-type MgFeNbO_5 became preferential, and at 1350°C , the intermediate phases were almost disappeared (corresponding to Fig. 1(b)). After a certain holding time at a high temperature

4. Conclusions

In this report, self-organized formation of spherical porous granules (SPGs) in MgO-Fe₂O₃-Nb₂O₅ system was presented. Only by the heat-treatment of the MgCO₃ (basic)-α-Fe₂O₃-Nb₂O₅ mixed powder, SPGs with 3-D network structure, typically 50-100 μm in diameter, were obtained. The mechanism of porous sphere formation is probably attributable to (1) local liquid phase formation by multiphase eutectic reactions and (2) limited sinterability of anisotropic pseudobrookite-type grains.

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Figure Captions

Fig. 1 SEM images of (a) the MgCO_3 (basic)- $\alpha\text{-Fe}_2\text{O}_3$ - Nb_2O_5 mixed powder and (b) its heat-treated-only product (SPGs) at 1350°C ; (c) digital optical microscope image of SPGs.

Fig. 2 Lower magnification SEM images of the heat-treated products from the MgCO_3 (basic)- $\alpha\text{-Fe}_2\text{O}_3$ - Nb_2O_5 mixed powder.

Fig. 3 Higher magnification SEM micrographs of the heat-treated products from the MgCO_3 (basic)- $\alpha\text{-Fe}_2\text{O}_3$ - Nb_2O_5 mixed powder.

Fig. 4 HT-XRD patterns for the MgCO_3 (basic)- $\alpha\text{-Fe}_2\text{O}_3$ - Nb_2O_5 mixed powder. Mg : Fe : Nb was 1:1:1 in mole fraction. The top pattern was taken at room temperature after cooling. Patterns at 100° , 200° , 300° , 400° , 1050° , 1150° and 1250°C are not shown here.