Effect of Tween 20 Concentration on Macropore Formation in Spherical Diopside Particles

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Abstract
We previously succeeded in fabrication of spherical diopside particles having a uniformly and continuously macroporous structure by heat treatment of silica gel particles impregnated with an aqueous mixed solution of Ca(NO3)2 and MgCl2 above 900°C [Y. Nakamura, et al., J. Ceram. Soc. Jpn., 112, 133 (2004)]. In preparing the mother silica gel particle, the nonionic surfactant, Tween 20, was employed as an emulsifier for maintaining an O/W emulsion of tetraethyl orthosilicate. In this study, we investigate influence of Tween 20 concentrations on macropore formation of spherical diopside particles. When silica gel particles prepared at Tween 20 concentration ranged from 0.75 to 15 wt% is impregnated with the Ca(NO3)2 and MgCl2 aqueous mixed solution and is heat-treated at 950°C, spherical diopside particles having macroporous structure can be fabricated. However, silica gel particles produced at 0 and 25 wt% of Tween 20 are largely unable to condense Si-OH groups and cannot crystallize to form diopside by the heat treatment, forming no macroporous structure. The nonformation of the macroporous structure in the case of the silica gel particle produced at 0 and 25 wt% of Tween 20 may be attributable to the fact that the silica gel particle is difficult for the silica gel particle to be impregnated with the Ca(NO3)2 and MgCl2 aqueous mixed solution.

Key-words: Spherical diopside particle, Macropore formation, Silica gel particle, Nonionic surfactant, Viscous fluid
acid (HCl), cyclohexane, 2-methyl-2-butanol, 25% ammonia solution, calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O), and magnesium chloride hexahydrate (MgCl₂·6H₂O) were all purchased from Wako Pure Chemical Industries, Ltd., and were used without further purification. Polyoxethylene sorbitan monolaurate (Tween 20) was purchased from ICN Biomedicals Inc., and was used as a surfactant.

2.2 Preparation of spherical diopside particle with macropore structure

Spherical diopside particles with a macropore structure were prepared by the method reported in our previous paper, as shown in Fig. 1[18]. 2.50×10⁻¹ kg of TEOS was mixed with a solution consisting of 6.82×10⁻² kg of ethanol, 2.16×10⁻² kg of distilled water, and 9.40×10⁻³ kg of HCl-ethanol solution, and the mixture was heated at 60°C for 30 min. to yield partly hydrolyzed TEOS. The partly hydrolyzed TEOS containing solution was then heated at 110°C for 2 hr and 150°C for 2 hr to remove the solvent completely. After stirring at 1000 rpm for 15 min., 3.88×10⁻² kg of the remaining solution containing 5.60×10⁻³ kg of cyclohexane and 2.00×10⁻² kg of 2-methyl-2-butanol was added dropwise into an aqueous mixture consisting of 4.34×10⁻¹ kg of distilled water, 1.35×10⁻² kg of ethanol, and various concentrations of Tween 20 (0, 0.75, 5.0, 15, and 25 wt%), and the mixture was stirred for 45 min. to form O/W emulsion. When 1.06×10⁻¹ kg of 25 wt% aqueous ammonia solution was added into the emulsion, spherical silica gel particles were immediately formed. The gel dispersion was stirred for 5 hr and was then aged for 10 hr to precipitate the gel at the bottom of a container. The supernatant was removed by decantation, and the gel was separated by suction filtration and was dried at 110°C for 5 hr after washing with ethanol. 2.00×10⁻³ kg of the dried spherical silica gel particles was mixed with 5.00×10⁻³ kg of distilled water containing 3.98×10⁻³ kg of Ca(NO₃)₂·4H₂O and 3.44×10⁻³ kg of MgCl₂·6H₂O. The silica gel was dried at 110°C for 24 hr and was heated at a rate of 20°C/min towards 950°C, at which the gel was held for 2 hr.

2.3 Characterization of spherical diopside particle with macropore structure

Morphology of spherical diopside particles was observed by scanning electron microscopy (SEM; JSM-5500LV, JEOL). Crystal structure and phase of spherical diopside particles were identified by X-ray powder diffractionmetry (XRD; RINT 2500VHF, RIGAKU) with CuKα radiation and by Fourier transform infrared spectroscopy (FT-IR; FT/IR-460 Plus, JASCO) with the KBr method. Pore characterization of silica gel particles and spherical diopside particles was measured by a surface area analyzer (SA3100, Beckman Coulter, Inc.) using N₂ gas and a mercury-injected porosity meter (Autopore 9500, SHIMAZU), respectively.

3. Results and Discussion

Figs. 2 a-e show SEM photographs of heat-treated silica gel particles prepared at Tween 20 concentration ranged from 0 to 25 wt%. A macroporous texture is observed throughout
papers\textsuperscript{22,23}). In particular, the larger peaks at 29.9 and 35.5 degrees correspond to (221) and (201) of diopside crystal, respectively. In using the Tween 20 concentration of 0 and 25 wt%, however, the silica gel particle is largely unable to crystallize to form diopside, and several unknown peaks (crosses) also appear in addition to the peaks characteristic to diopside crystal.

We measured XRD patterns of heat-treated silica gel particles impregnated with either Ca(NO\textsubscript{3})\textsubscript{2} or MgCl\textsubscript{2} aqueous solution (Tween 20 concentration: 0.75 wt%). The XRD patterns of heat-treated silica gel particles prepared with 0 and 25 wt% of Tween 20 that are represented in Fig. 3 are also shown. ■: peak originated from silica gel particles heat-treated with MgCl\textsubscript{2} alone, ●: peak assigned to diopside crystal.

The XRD patterns of heat-treated silica gel particles heat-treated with either Ca(NO\textsubscript{3})\textsubscript{2} or MgCl\textsubscript{2} (Tween 20 concentration for preparation of silica gel particles: 0.75 wt%). The XRD patterns of heat-treated silica gel particles prepared with 0 and 25 wt% of Tween 20 that are represented in Fig. 3 are also shown. ■: peak originated from silica gel particles heat-treated with MgCl\textsubscript{2} alone, ●: peak assigned to diopside crystal.

We measured XRD patterns of heat-treated silica gel particles impregnated with either Ca(NO\textsubscript{3})\textsubscript{2} or MgCl\textsubscript{2} aqueous solution (Tween 20 concentration: 0.75 wt%). The result is represented in Fig. 4 along with the XRD patterns of the heat-treated silica gel particle prepared at 0 and 25 wt% of Tween 20, shown in Fig. 3. As can be seen from this figure, it is suggested that the unknown peaks at 24.0 and 31.2 degrees (closed squares) of the XRD pattern in the case with 0 and 25 wt% of Tween 20 are originated from crystals of the silica gel particle heat-treated with MgCl\textsubscript{2} alone, assigned to forsterite (Mg\textsubscript{2}SiO\textsubscript{4}), and clinoenstatite and/or enstatite (MgSiO\textsubscript{3}) crystals.

FT-IR spectra of the same heat-treated silica gel particles is shown in Fig. 5. There is a broad absorption peak of an amorphous silica gel phase around 1,100 cm\textsuperscript{-1} assigned to Si-O group before the heat treatment. When the silica gel particle prepared at Tween 20 concentration ranged from 0.75 to 15 wt% is heat-treated, three distinct absorption peaks appear at 884, 968, and 1,071 cm\textsuperscript{-1}. These peaks correspond to an asymmetric stretching vibrational mode
As mentioned in Introduction, the inorganic salts, Ca(NO₃)₂ and MgCl₂, play an important role in forming the macropores in the spherical diopside particle. The inorganic salts transform the silica gel amorphous phase into viscous fluid under high temperature treatment. The irregular mesopores in the viscous fluid, which originate from the formation of the silica gel particle by the sol-gel method, aggregate with one another to minimize excess surface energy between the pore and the viscous fluid, leading to the formation of the macroporous structure, as shown in Figs. 2 b-d. Therefore, the penetration of the aqueous inorganic salt solution into the silica gel particle is considered to be important for the formation of the macroporous structure.

When the silica gel particle prepared at the Tween 20 concentration ranged from 0.75 to 15 wt% was added to the Ca(NO₃)₂ and MgCl₂ mixed solution, the solution easily permeated the silica gel particle. On the other hand, the mixed solution hardly permeated the silica gel particle prepared at 0 and 25 wt% of Tween 20. We then estimate an absorption capacity of the Ca(NO₃)₂ and MgCl₂ mixed solution in the silica gel particle. The result is shown in Fig. 6. Here, the absorption capacity is defined as the rate of the absorption weight of the mixed solution to the weight of the silica gel particle. The absorption capacity increases with increasing Tween 20 concentration and reaches the maximum at 5 wt% of Tween 20. This finding reveals that the solution hardly permeates the silica gel particle produced at 0 and 25 wt% of Tween 20, as compared with that from 0.75 to 15 wt% of Tween 20; thereby, the silica gel particle prepared with 0 and 25 wt% of Tween 20 cannot transform into viscous fluid by the heat treatment, forming no macroporous texture.

As a result from a series of our observations, we consider that there is the optimal Tween 20 concentration ranged from 0.75 to 15 wt% to produce the spherical diopside particle having the macropore structure.

Fig. 5 FT-IR spectra of heat-treated silica gel particles prepared with various concentrations of Tween 20.

Fig. 6 Change in absorption capacity of Ca(NO₃)₂ and MgCl₂ mixed solution into silica gel particles with Tween 20 concentration.
of Tween 20. The total pore volume of the silica gel particle is almost equal to 1.5 mL/g at the Tween 20 concentration between 0 and 15 wt%, and is the smallest at 25 wt% of Tween 20. From this result, therefore, the smallest total pore volume causes less permeation of the inorganic salt solution into the silica particle prepared at 25 wt% of Tween 20.

Fig. 6 also indicates that the aqueous Ca(NO₃)₂ and MgCl₂ mixed solution hardly permeates the silica gel particle prepared at 0 wt% of Tween 20 (without Tween 20), as well as that with 25 wt% of Tween 20. As can be seen from Fig. 7, to the contrary, the total pore volume of the silica gel particle is about 3 times larger at 0 wt% of Tween 20 than at 25 wt% of Tween 20. Thus, we need to take account of other factors, except for total pore volume, to contribute to less permeation of the inorganic salt solution into the silica gel particle prepared without Tween 20.

In general, penetration of liquid into small pores is induced by capillarity force of the pore; the greater capillarity force, the larger liquid penetration. Capillarity force of small pores for liquid, \( \Delta F \), is expressed as the following equation:

\[
\Delta F = \frac{2 \gamma \cos \theta}{r_p}
\]

Here, \( \gamma \), \( \theta \), and \( r_p \) correspond to surface tension of the liquid, contact angle of the liquid to inner walls of the pore, and radius of the pore, respectively. Eq. (1) then shows that \( \Delta F \) increases with a decrease in the contact angle.

As mentioned in Experimental procedure, the mother silica gel particle was washed with ethanol before the addition of the aqueous Ca(NO₃)₂ and MgCl₂ mixed solution. In this way, not all surfactants, Tween 20, can be removed from the silica gel particle. Indeed, we find the absorption peak coming from C-H stretching vibration of Tween 20 in the IR spectra of the silica gel particle prepared at the Tween 20 concentration above 15 wt% (data not shown). We speculate that there remains Tween 20 in the silica gel particle prepared at 0.75 and 5.0 wt% of Tween 20. The remaining surfactant may then reduce the contact angle of the aqueous inorganic salt solution to the inner wall of the mesopore in the silica gel particle. In the silica gel particle prepared with 0 wt% of Tween 20, however, the contact angle may be larger because no surfactant is used. Hence, the larger contact angle makes the capillarity force smaller, leading to less permeation of the aqueous inorganic salt solution into the silica gel particle prepared at 0 wt% of Tween 20, as shown in Fig. 6.

4. Conclusion

We investigated the effect of the Tween 20 concentration on the macropore formation of the spherical diopside particle. When silica gel particles prepared at Tween 20 concentration ranged from 0.75 to 15 wt% is heat-treated with Ca(NO₃)₂ and MgCl₂ at 950°C, spherical diopside particles having macroporous structure can be fabricated. However, the silica gel particle produced at 0 and 25 wt% of Tween 20 is largely unable to condense Si-OH groups and cannot crystallize to form diopside by the heat treatment; furthermore, no macroporous structure is formed. The non-formation of the macroporous structure in the case of the silica gel particle produced at 0 and 25 wt% of Tween 20 may be attributable to the fact that it is difficult for the silica gel particle to be impregnated with the Ca(NO₃)₂ and MgCl₂ aqueous mixed solution.

References

多孔質ディオプサイド微粒子の調製に及ぼす非イオン系界面活性剤Tween 20濃度の影響

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要 旨
われわれは、Ca(NO_3)_2およびMgCl_2水溶液を含浸させたシリカゲル微粒子を900℃で焼成することにより、均一な連続的マクロ孔を有するディオプサイド微粒子の合成に成功した（Nakamura, et al.: J. Ceram. Soc. Jpn., 112, 133 (2004)）。本研究では、シリカゲル微粒子調製の際に利用した非イオン系界面活性剤であるTween 20の濃度が、ディオプサイド微粒子中のマクロ孔の形成に及ぼす影響について検討した。その結果、Tween 20濃度0.75 〜 15 wt%において、均一な連続的マクロ孔が形成することが確認された。しかし、Tween 20濃度0（無添加）および25 wt%においては、均一な連続的マクロ孔の形成は認められなかった。これらは、Tween 20濃度0（無添加）および25 wt%において調製されたシリカゲル微粒子は、Ca(NO_3)_2およびMgCl_2水溶液を十分に含浸できないためと考えられる。

キーワード：球状ディオプサイド微粒子、マクロ孔形成、シリカゲル微粒子、非イオン系界面活性剤、粘性流体