Paper

Fabrication of 12CaO·7Al$_2$O$_3$ powders with high specific surface area by sol–gel and ball-milling method

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12CaO·7Al$_2$O$_3$ (called as C12A7) is composed of [Ca$_{24}$Al$_{28}$O$_{64}$]$^{4+}$ cages in which oxide anions are entrapped. Recent studies have revealed that the outstanding characteristics appear by exchanging the free oxide anions in the cages by various other anion species. In the present report, in order to enhance the oxidative catalytic activity of C12A7 by the encaged oxygen radicals, we synthesized C12A7 fine powders with high-specific surface area by sol–gel method and subsequent ball-milling. Aluminum sec-butoxide, calcium nitrate tetrahydrate, absolute ethanol, 1 M hydrochloric acid, and ethyl 3-oxobutanate were used as raw materials. The obtained precursor solution was dried at 100°C for 24 h, and the product obtained was annealed at 900°C in O$_2$ atmosphere. Planetary ball milling was subsequently applied to the C12A7 powders. The XRD measurements revealed that the synthesized sample was a single phase C12A7. The BET specific surface area of the ground samples was 48.9 m^2/g (24 h ground) and 17.3 m^2/g (36 h ground) for those prepared by sol–gel method and by solid state reaction, respectively. The possibility was thus demonstrated on the synthesis of C12A7 fine powders with higher specific surface area by sol–gel method and subsequent planetary ball-milling.
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1. Introduction

12CaO·7Al$_2$O$_3$ (called as C12A7) has attracted attention as functional ceramics. The crystal structure of C12A7 is cubic with lattice constant 1.199 nm. The unit cell of the crystal is composed of the "cages", [Ca$_{24}$Al$_{28}$O$_{64}$]$^{4+}$, and the "oxide anions clathrated in the cages".[1)–4)] Though the crystal is a stable ceramic well known as a constituent of aluminum cements, the recent studies have revealed that the outstanding characteristics appear by exchanging the oxide anions in the cages (called as free oxide ions) by various other anion species.[5)–8)]

When oxygen radicals, O$^-$, encaged in the C12A7 cage, C12A7 shows a high oxidative power. Dong et al. reported that a direct oxidation of benzene using C12A7–O$^-$ yields phenol.[9)] Wang et al. also reported a production of hydrogen by catalytic steam reforming of bio-oil using C12A7–O$^-$.[10)] Yang et al. reported partial oxidation of methane using C12A7–O$^-$.[11)] Even though C12A7 has a high potential for oxidation catalysis, much work has been done on the fabrication route for C12A7 as catalysts, i.e. nano/microparticles with high specific surface area. Most of publications regarding C12A7 oxidizing catalysts have been based on bulk or powders basically fabricated by solid state reaction (and subsequent ball-milling). The solid state reaction is a conventional and simple method but needs high reaction temperatures above 1200°C and long reaction time.[9)–11)] Such high temperatures are undesirable from the viewpoint of energy consumption, and also possibly cause a crucial problem: drastically reducing specific surface area of the C12A7 catalysts. When the powders are heated at high temperatures for increasing

the solid state reaction rate, the grains also grow and the grain size increases. Thus it can be said that the solid state reaction method is not appropriate for obtaining powders with high specific surface area. One of the potential methods for fabricating powders with high specific surface area is the solution process, such as a sol–gel method, which does not require high annealing temperatures. The sol–gel method can achieve homogeneous compositions at low temperatures, and can control the morphology of the products (fine particle, thin firm, etc.).[12),13)]

In the present paper, in order to enhance an ability of C12A7 as an oxidation catalyst by caused by the encaged oxygen radicals, we synthesized C12A7 fine powder with high-specific surface area by sol–gel method. The powder showed much higher specific surface areas than the products by solid state reaction by subsequent ball-milling.

2. Experimental

Aluminum sec-butoxide [Al(OBu^s)$_3$, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan] and calcium nitrate tetrahydrate [Ca(NO$_3$)$_2$·4H$_2$O, 99.9%, Wako Pure Chem. Ind. Ltd., Tokyo, Japan] were used as starting reagents for C12A7 precursor solutions. Ethyl 3-oxobutanate (CH$_3$COCH$_2$COOC$_2$H$_5$, 98.0%, Wako Pure Chem. Ind. Ltd., Tokyo, Japan) was used as a chelating agent.[14)] Absolute ethanol was used as a solvent. 1 M hydrochloric acid (HCl, Kanto Chem. Ind. Ltd., Tokyo, Japan) was used a deflocculant.

The aluminum precursor solution was prepared by the following procedure. Aluminum sec-butoxide and ethyl 3-oxobutanate were mixed, and the mixture obtained was stirred for 30 min at 50°C (the solution became uniform and clear). The solution thus obtained was added in absolute ethanol. Distilled water and 1 M hydrochloric acid were added, and the resulting

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solution was stirred for another 2 h at 60°C. The calcium precursor solution was prepared by the following procedure. Calcium nitrate tetrahydrate was dehydrated at 150°C for 1 h. The products were subsequently dissolved in absolute ethanol, and the mixture was stirred for 1 h. The aluminum and calcium precursor solutions thus prepared were mixed to obtain the C12A7 precursor solution. The obtained precursor solution was dried at 100°C for 24 h and annealed at 700–900°C in O_2 atmosphere.

C12A7 powders were also prepared by solid state reaction for comparison, where the mixture of $CaCO_3$ and Al_2O_3 powders with a molar ratio of 12:7 was annealed at 1300°C for 6 h in air.

Planetary ball milling (puluerisette-7, FRITSCH GmbH, Germany) was subsequently applied to the C12A7 powders. The milling was performed with using zirconia balls of 0.5 mm in diameter in absolute ethanol. In order to estimate the optimum milling time duration, the milling time duration was varied from 12 to 48 h with a fixed grinding rate of 150 rpm.

A Fourier transform infrared spectrometer (FTIR8500, SHIMADZU Ltd., Kyoto, Japan) was used to investigate the chemical bonds formed in the dried gel. The assignment of absorption bands was based on Ref. 14.

The thermal behavior and the weight change during annealing were investigated on the dried gel by thermogravimetry and differential thermal analysis (TG–DTA) (Model Thermo plus TG8120, Rigaku Ltd., Tokyo, Japan). The crystal structure of the obtained powders was identified by X-ray diffraction (XRD) (Model D8 Advance, Brucker AXS GmbH, Germany). The microstructure of the obtained powders was investigated by scanning (Model JSM-5510SV, JEOL Ltd., Tokyo, Japan) and transmission electron microscopy (TEM) (Model JEM-2100F, JEOL Ltd., Tokyo, Japan). The particle size distribution was measured by dynamic light scattering (Model Photal SELS-800Y, Otsuka Electronics Co., Ltd., Osaka, Japan) using absolute ethanol as solvent. The specific surface area of the powders was measured by BET analysis using nitrogen gas adsorption.[15]

3. Result and discussion

Figure 1 shows the FTIR spectra of the dried gel. Characteristic absorption bands were detected at 1525 and 1180 cm^{-1}, which are assigned to the C–C vibration of a six membered ring of the complex and to the –C–C–O stretching vibration, respectively. This obviously shows that the aluminum sec-butoxide was chelated by ethyl 3-oxobutanate, by which the dried gel became stable compared to that without using chelating agent.
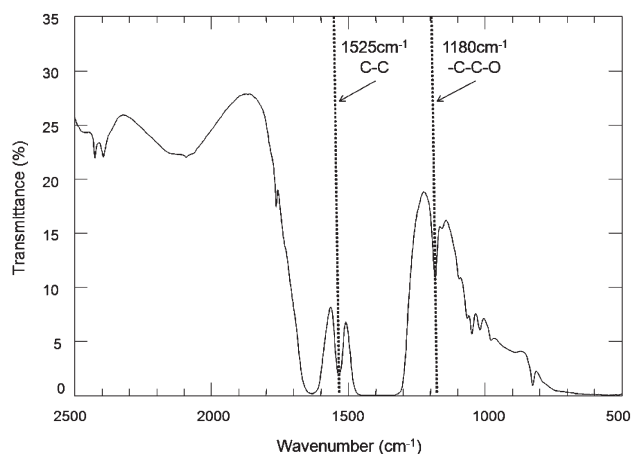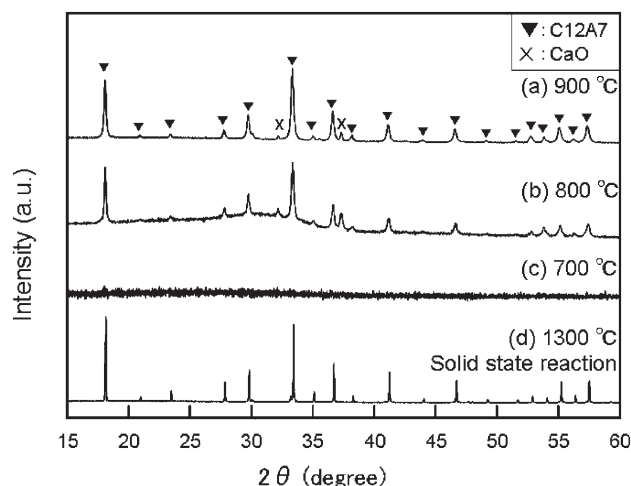

Fig. 1. FTIR spectra of the dried gel.

Fig. 2. X-ray diffraction patterns of the powders synthesized by the sol–gel method and annealed at (a) 900, (b) 800 and (c) 700°C, and (d) those synthesized by the solid state reaction at 1300°C.

Figure 2 show the XRD patterns of the powder samples synthesized by the sol–gel method at various annealing temperatures and by the solid state reaction. The samples synthesized by either method [Figs. 2(a) and 2(d)] were single phase C12A7. The powder sample annealed at 900°C was single phase C12A7, whereas the those at 700 and 800°C contained CaO and amorphous phases [Figs. 2(b) and 2(c)]. These results indicate that the crystallization temperature of C12A7 is below 800°C. In most cases, the solid state reaction requires high temperatures above 1200°C for obtaining single phase C12A7. The present results indicate that the sol–gel method drastically reduces the temperature for synthesizing C12A7 powders. Based on these results, the optimum annealing temperature was determined to be 900°C for the sol–gel method. In the following sections, the annealing temperature was fixed at 900 and 1200°C for the sol–gel method and the solid state reaction, respectively.

Figures 3(a) and 3(b) show the XRD patterns of the samples prepared by the sol–gel method and the solid state reaction, respectively, measured after the ball milling. It was confirmed that both samples obtained by the sol–gel method and the solid state reaction held the C12A7 crystal structure even after the ball milling, although amorphous phases seem to be slightly increased in amount. The amorphous phases might be decreased by milling under milder conditions at lower rotation speeds, with lighter weight balls and so on.

Figure 4 shows the BET specific surface area of the samples obtained by the sol–gel method and solid state reaction at various milling time duration. The specific surface area increased with increasing milling time for both samples. The maximum specific surface area was 48.9 m^2/g (sol–gel derived sample with 24 h ground) and 17.3 m^2/g (sample by solid state reaction method with 36 h ground). It is worth noting that the specific surface area stayed at the maximum values even when further grinding was applied. This result indicates that the highest specific surface area of the sol–gel derived C12A7 powders is not achievable by the solid state reaction. The highest specific surface area, 48.9 m^2/g, is comparable to those reported on other oxidation catalysts (about 30–130 m^2/g).[16]–[19] In the following description, "ground samples" indicate the samples ground under the optimum conditions, i.e. ground for 24 and 36 h for the samples prepared by the sol–gel method and by the solid state reaction, respectively.
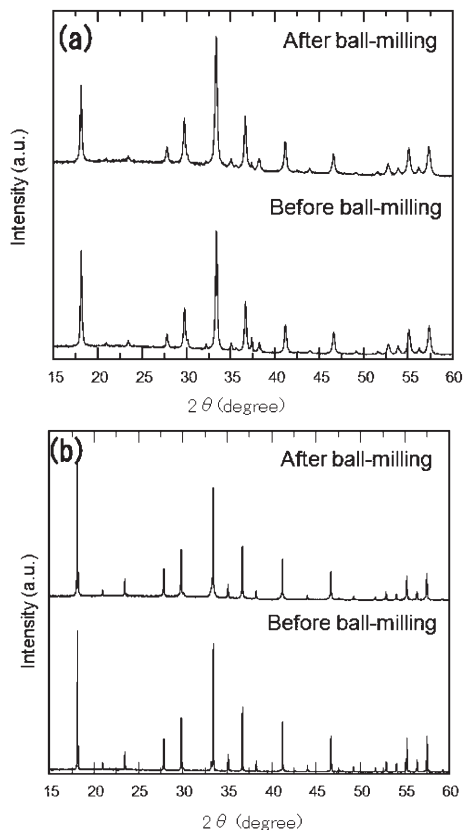
Fig. 3.   XRD patterns of the C12A7 powders before and after the ball milling obtained by (a) the sol–gel method and (b) the solid state reaction (Milling time: 24 h for the sol–gel method sample, 36 h for the solid state reaction sample). No obvious peak appeared after the ball milling for both of the samples.
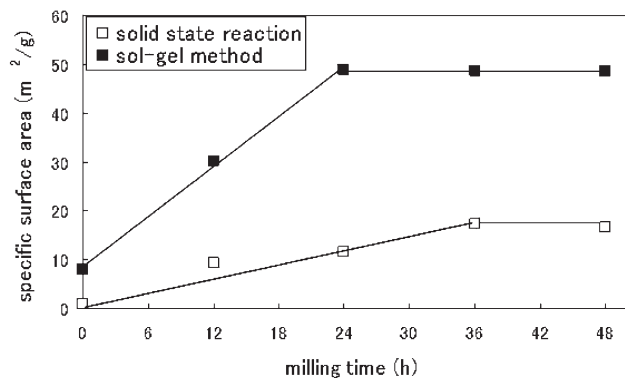

Fig. 4.   Specific surface area of the samples with various milling times.

Fig. 5.   Particle size distribution in the C12A7 powders (a): synthesized by the sol–gel method and measured before the ball-milling (24 h), (b): synthesized by the sol–gel method and measured after the ball-milling, (c): synthesized by the solid state reaction and measured before the ball-milling, (d): synthesized by solid state reaction and measured after the ball-milling (36 h).

Figure 5 shows the particle size distribution in the powder samples. The particle size of the C12A7 powders synthesized by the sol–gel method was distributed in 150–1200 nm (the average particle size: 357.5 nm) before the ball-milling [Fig. 5(a)], whereas that after ball-milling [Fig. 5(b)] became narrower in distribution in 100–450 nm (the average particle size: 193.1 nm). On the other hand, the C12A7 powders synthesized by the solid state reaction had two average particle sizes, 279 and 2180 nm, before ball-milling [Fig. 5(c)], which were reduced to 193 and 879.2 nm, respectively, by the ball milling [Fig. 5(d)]. It is obviously shown that the ball-milling reduces the average
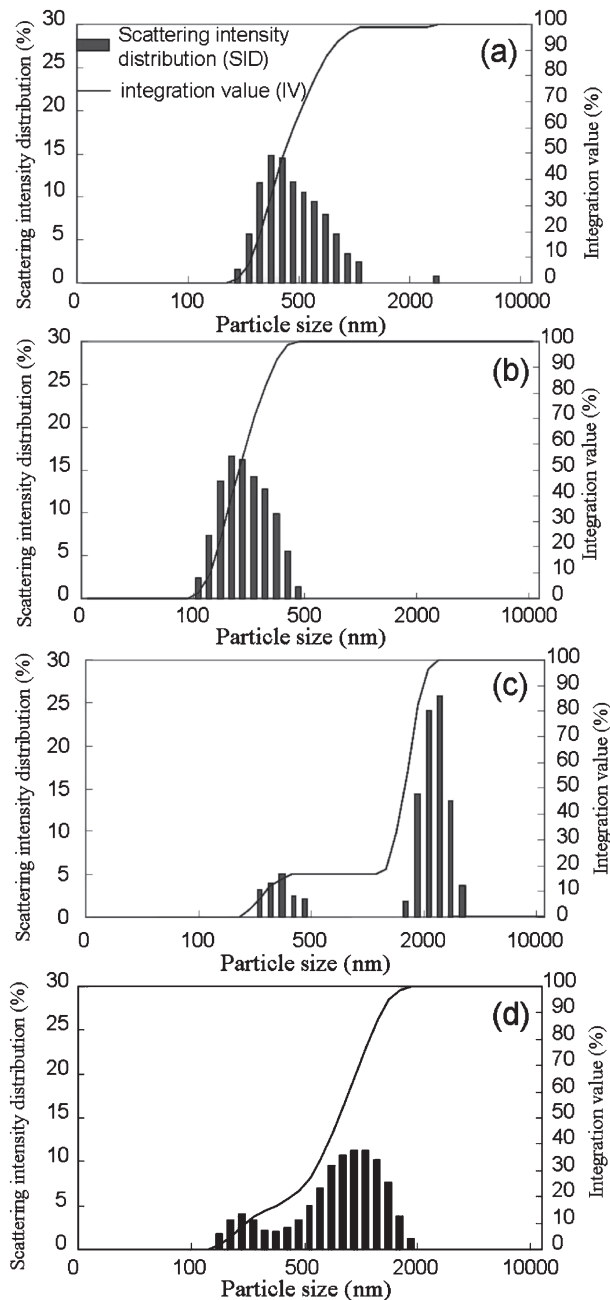
particle size for both samples. It is worth noting that the powders synthesized by the sol–gel method had the small average particle size and the relatively narrow particle size distribution compared to those prepared by the solid state reaction. These results imply that the sol–gel method is suitable for synthesizing C12A7 powders with small particle size.

In order to investigate why the different grinding behavior appeared in the two samples, the microscopic and crystallographic analyses were applied. **Figure 6** shows the TEM images of the powder samples. The C12A7 powders synthesized by the sol–gel method consisted of aggregates of tiny primary particles
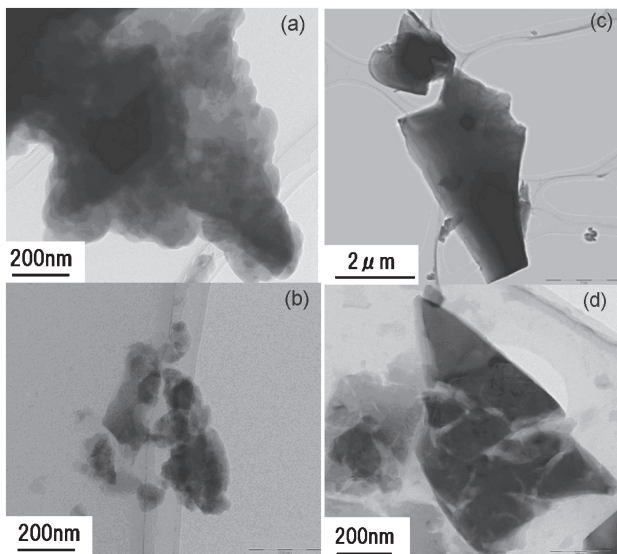
Fig. 6. TEM images of the C12A7 powders (a) synthesized by the sol–gel method and measured before the ball-milling, (b) synthesized by the sol–gel method and measured after the ball-milling, (c) synthesized by the solid state reaction and measured before the ball-milling, and (d) synthesized by the solid state reaction and measured after the ball-milling.

Table 1. Average crystallite size calculated by Rietveld analysis using TOPAS software

Method	Crystallite diameter (nm)	
	Before ballmiling	After ballmiling
Sol–Gel method	29.3	26.0
Solid state reaction	275.5	136.6

of several tens nm before the ball-milling [Fig. 6(a)]. The ball-milling reduced the size of the aggregates drastically with the crystallite size maintained although the primary particles still formed small aggregates of 100 to 500 nm in size as shown in the Fig. 6(b). On the other hand, the C12A7 powders synthesized by the solid state reaction consisted of large grains with several micrometers before the ball-milling [Fig. 6(c)] whereas the grains were cracked and the size decreased by the ball-milling [Fig. 6(d)]. These behaviors were confirmed by the XRD and subsequent Rietveld analysis as well (**Table 1**).[20] The average crystallite size of the sol–gel derived sample before ball-milling was 29.3 nm, which was much smaller than that by the solid state reaction, 275.5 nm. The grinding effect on the crystallite size was almost negligible in the sol–gel derived sample, whereas the crystallite size of the sample by the solid state reaction was decreased to almost 50% by the grinding. The main reason for this different grinding effect seems to lie in the primary particle size. The agglomerates composed of tiny primary particles seen in the sol–gel derived sample can be deagglomerated by the grinding, whereas the large grains seen in the solid state reaction sample were ground rather than deagglomerated. It is easily understood that the agglomerates composed of tiny particles are readily deagglomerated into small particles, which results in the high specific surface area. This result definitely indicates that the sol–gel method has a quite high advantage for obtaining the high specific surface area C12A7 powders.

4. Summary

Single phase C12A7 powders were successfully synthesized by the sol–gel method through annealing at 900°C. The primary particle size (29.3 nm estimated by Rietveld analysis) of the C12A7 powders obtained by the sol–gel method was several hundred nanometers and they were composed of agglomerates of several tens nanometers. The agglomerate was deagglomerated by subsequent ball-milling and the highest specific surface area of 48.9 m^2/g (24 h ground) was achieved. On the other hand, the highest specific surface area of the C12A7 powders synthesized by the conventional solid state reaction was 17.3 m^2/g. The TEM and XRD analyses implied that the difference in the grinding effect between these two samples lies in the different primary particle sizes; the deagglomeration for tiny primary particles (the sol–gel derived sample) and the crushing for large primary particles (the sample prepared by the solid state reaction). It was indicated that the sol–gel method is a desirable way to synthesize C12A7 powders with high specific surface area.

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