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Esterification of tripalmitin using calcined scallop shell as a heterogeneous basic catalyst

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Abstract

Calcined waste scallop shell (*Patinopecten yessoensis*) was used as a basic heterogeneous solid catalyst for the transesterification of tripalmitin as a model triglyceride for assuming biodiesel production. The scallop shell was pulverized and calcined at 900 and 1000 °C for 4 hours. Calcined reagent calcium carbonate was also used as a control catalyst. The transesterification experiments were carried out at 30°C with varying catalyst dosage and calcination conditions. In the most experimental condition, the yield reached ca. 90 % within 8-10 hours. The overall reaction rate constant, *k*, was determined by simple first-order reaction kinetics. The calcined catalyst was characterized using SEM, EDS, and XRD analysis. The number of basic active sites on the surface was determined by titration with benzoic acid. A linear relationship between *k* and the number of the basic active sites was obtained. The time course of the concentration of the products could be estimated using this relationship.

KEYWORDS: Calcium oxide; Waste scallop shell; Transesterification; Biodiesel; Fatty acid methyl ester

1 INTRODUCTION

Biodiesel production has attracted much attention during the last two decades as a renewable and environmentally friendly fuel[1-7] from the viewpoints of depletion of fossil fuels, concerns about environmental problems, and effective utilization of biomass resources. Biodiesel is chemically a fatty acid methyl ester (FAME). In the last two decades, many studies have been reported about the utilization of waste cooking oil for biodiesel production[8-10], and other resources for biodiesel production have also been reported, such as vegetable oil[11], plants[12,13], animal fat[1,14,15], microalgae[16], fish[1,17,18], calcium-rich food[19] and so on. We are proceeding with a study of the utilization of lipids obtained from fisheries industrial waste to biodiesel production[20].

The transesterification method has been generally employed in biodiesel production by using a homogenous[21,22] or a heterogeneous[23-25] catalyst. The majority of biodiesel production processes often use homogeneous base catalysts such as alkaline metal alkoxides[21] and hydroxides[24]. Homogeneous catalysts lead to better reaction efficiency than heterogeneous catalysts, however, the separation of homogeneous catalysts is too difficult and remarkably expensive[1].

Many researchers have reported that basic solid catalysts are effective for the ester exchange reaction of triglycerides, and calcium oxide (CaO) is a particularly good catalyst for this purpose[11-14]. The main component of seashells is calcium carbonate ($CaCO_3$). It is also known that $CaCO_3$ converts to CaO at temperatures above 600 °C. Thus CaO is obtained by calcined seashells at a high temperature of over 750 °C[26].

We focused on the utilization of waste seashells. CaO can be prepared from waste shells, which are the largest amount of fisheries waste. In Japan, scallop farming has been one of the major maricultures. For example, the annual production of cultured scallops was ca. three

hundred ninety thousand tons in Hokkaido prefecture in 2019, on the other hand, the waste shells were ca. fourteen hundred thousand tons in 2019. The waste scallop shell is usually stacked on the roadside, and becoming a serious environmental problem. The useful utilization of waste scallop shells is important to solve the environmental problem.

Many studies have been conducted on the production of biodiesel using calcined seashells as catalysts[11-14], for example, waste shells of oyster[27], mollusk[28], coral fragment[29], scallop[30,31], clam shells[32,33], mussel and cockle[34], Malleus malleus[35], conch shells[36] and so on. However, most of these studies were conducted under limited conditions, and they were experimental screening studies using different types of raw materials and catalysts. The quantitative understanding of the properties and performance of calcined shells as catalysts is very important for the design and optimal operation of the reaction system in industrial applications from the viewpoint of chemical engineering.

In this study, we employed the calcined waste scallop shell as the catalyst of the transesterification reaction. We quantitatively investigated the relationship between the catalytic efficiency of the calcined waste scallop shell and the number of active sites on the calcined scallop shell surface using a kinetics parameter, the overall rate constant of transesterification reaction rate, as an indicator. Tripalmitin was used as a model triglyceride for the transesterification reaction. An understanding of the relationship is necessary for biodiesel production using calcined shells as catalysts to design and improve the reactor. We discussed and showed the estimation protocol using the relationship between the overall reaction rate constant and the number of the active sites on calcined catalysts.

2 EXPERIMNTAL

2.1 Materials

2.1.1 Scallop shell

Scallop shell was obtained from commercial markets or restaurants in Hakodate city, Japan. They were mostly captured at Funka bay (Hokkaido prefecture) and Mutsu bay (Aomori prefecture) in Japan.

2.1.2 Chemicals

Tripalmitine (97 %), methyl alcohol, ethyl alcohol, toluene, sodium, sulfate, acetic acid, phenolphthalein, and benzoic acid were purchased from Fujifilm Wako Pure Chemical Co. (Japan). Calcium oxide, calcium carbonate, hexane, diethyl ether, and silica particle (silica gel 60) were purchased from Kanto Chemical Co. Inc. (Japan). Molecular sieve 4A was purchased from Nakalai Tesque Inc. (Japan). All purchased reagents were used without further purification.

2.2 Preparation of calcined shell catalyst

The scallop shell was washed well with tap water and rinsed with distilled water. They were dried at room temperature for 24 hours. The shells were crushed into appropriate sizes (2-3 cm) by using a hammer. 10 g of the crushed shell pieces were pulverized by a ceramic ball mill for 24 hours. 2 g of the pulverized shell power was taken into a platinum plate and

calcined at 900 or 1000 °C for 4 hours in a muffle furnace, and then it was cooled in the muffle furnace. All calcinations in this study were conducted in the presence of air without any gas replacements. The powder was stored in a 5 mL polyethylene sample bottle. The air in the bottle was replaced with nitrogen gas and the bottle was stored in a desiccator. To compare with a commercial product of calcium oxide, reagent grade calcium oxide was also calcined in the same manner described above. The active sites on the catalyst surface were determined by titration with benzoic acid[37,38]. The particle size distribution was measured using a laser particle size analyzer (HORIBA LA-300, Japan). The particle morphology was observed using scanning electron microscopy (SEM, JSM6010LA, JEOL Ltd., Japan). The surface composition of the elements was measured using energy-dispersive X-ray spectroscopy (EDS) which is equipped with SEM instrumentation. The X-ray diffraction pattern was recorded an X-ray diffractometer (XRD, MiniFlex, Rigaku co., Japan). Hereafter, the catalysts derived from reagents and shells are written as C_{RE} and C_{SS}, and the calcination temperatures are written in the subscript, for example, $C_{RE\text{-}900}$ or $C_{SS\text{-}1000}$. The control catalysts without calcination are written as $C_{RE\text{-}0}$ and $C_{SS\text{-}0}$.

2.3 Procedure of transesterification experiment

The desired amount of calcined catalyst powder was taken into a 25 mL cylindrical glass vessel with a lid. Then, the desired amount of methanol-toluene mixture solution was also poured into the cylindrical vessel and stirred by using a magnetic stirrer for 2 hours. After this, the suspension with the vessel was decompressed by an aspiration for 5 min to deair the powder. A desired amount of tripalmitin was taken into another cylindrical glass vessel, and then the desired amount of the same composition of the methanol-toluene mixture solution was poured into the vessel to dissolve tripalmitin. Two vessels were set in a 30 °C water bath.

The tripalmitin solution was added to the suspension to adjust the initial concentration of tripalmitin to 25mL. We considered this addition as the start of the reaction. The suspension was stirred by using a magnetic stirrer for desired reaction time. After the desired reaction time, the suspension was filtered with a cellulose acetate membrane filter (average pore size 0.5 μm) to separate the catalyst, and 0.5 mL of acetic acid was added to the filtrate to stop the reaction completely. The products, methyl palmitate, and the unreacted tripalmitin were fractionated by thin-layer chromatography. After this, the amount of methyl palmitate was determined using gas chromatography (Shimadzu GC-2014, Japan).

3 RESULTS AND DISCUSSION

3.1 Characterization of calcined particles

To investigate the influence of the calcination temperature on the morphology and size of the catalyst, SEM images were taken. The typical images were shown in Figure 1. In both cases of C_{RE} and C_{SS}, it could be observed that the particle size was not quite different before calcination and calcined at 900 °C. In the case of $C_{RE\text{-}1000}$ and $C_{SS\text{-}1000}$, the particle size could be confirmed to be larger than that in the case of $C_{RE\text{-}0}$, $C_{RE\text{-}900}$, $C_{SS\text{-}0}$, and $C_{SS\text{-}900}$. As seen in Figures 1C and 1F, $C_{RE\text{-}1000}$ and $C_{SS\text{-}1000}$ were considered to be aggregated and sintered to each other by slight melting of the catalyst surface.

Figure 2 shows the size distribution of C_{RE} and C_{SS}. In the case of C_{RE}, the size distribution of $C_{RE\text{-}900}$ was mostly similar to that of $C_{RE\text{-}0}$. By comparison of the size distribution of $C_{RE\text{-}900}$ and $C_{RE\text{-}1000}$, the size distribution of $C_{RE\text{-}1000}$ shifted to a larger size region, and the size distribution range became slightly narrower. The mode diameters were 6.47 ($C_{RE\text{-}0}$), 5.77 ($C_{RE\text{-}900}$), and 9.32 μm ($C_{RE\text{-}1000}$). On the other hand, in the case of C_{SS}, the size distribution of $C_{SS\text{-}0}$ ranged widely (ca. 1-100 μm). It was observed that the size distribution range of $C_{SS\text{-}900}$ and $C_{SS\text{-}1000}$ quite narrowed and sharpened. The tendency of change in the size distributions of $C_{SS\text{-}900}$ and $C_{SS\text{-}1000}$ was mostly similar to these in the case of $C_{RE\text{-}900}$ and $C_{RE\text{-}1000}$. The mode diameters were 13.6 ($C_{SS\text{-}0}$), 14.8 ($C_{SS\text{-}900}$), and 17.2 μm ($C_{SS\text{-}1000}$). By comparison of the mode diameters of calcined C_{RE} and C_{SS}, the mode diameter of C_{SS} was 2.5 times ($C_{SS\text{-}900}$) and 1.8 times ($C_{SS\text{-}1000}$) larger than those of $C_{RE\text{-}900}$ and $C_{RE\text{-}1000}$. Sirisomboonchai et al. have reported that they observed the same melted and sintered phenomena over 1000 °C, and the most effective calcination temperature for the catalytic activity of calcined scallop shell was 900-1000 °C[30].

The elements component of C_{RE} and C_{SS} is summarized in Table 1. These values were obtained from measurement using EDS. It was confirmed that the difference in the calcination temperature did not affect element composition (C, O, Ca) and the fraction of CaO and $CaCO_3$ for C_{RE} and C_{SS}. However, the element composition and the fraction of CaO differed from C_{RE} and C_{SS}. As the result, the CaO fraction of C_{SS} was ca. 25 mol% lower than that of C_{RE}, and the $CaCO_3$ fraction of C_{SS} was ca. 25 mol% larger than that of C_{RE}.

XRD spectra pattern is shown in Figure 3. After the calcination at 900°C for 4 hours, major peaks of CaO are observed at 32.2, 37.4, 53.9, 64.2, and 67.4. Both spectra pattern of CaO of C_{RE} and C_{SS} was confirmed to be almost the same. These peak positions correspond to the CaO pattern (JCPDS: 00-037-1497), and those reported by some researchers[34,39,40]. Thus, the main component of C_{SS} would convert to calcium oxide (CaO).

3.2 Influence of catalyst dosage and calcination temperature on transesterification of tripalmitin

Figure 4 shows typical results of the time course of transesterification with varying dosages of C_{RE} and C_{SS}. These experiments were conducted in a 30°C water bath using $C_{RE\text{-}900}$ and $C_{SS\text{-}900}$ as catalysts. The ordinate, C_{MP}, corresponds to the concentration of methyl palmitate as a product. As the increase in the catalyst dosage of both $C_{RE\text{-}900}$ and $C_{SS\text{-}900}$, the degree of increase in methyl palmitate also became larger. Since the initial concentration of tripalmitin was set to 3.0×10^{-3} mol/L, the maximum concentration of methyl palmitate could become 9.0×10^{-3} mol/L stoichiometrically. C_{MP} reached the maximum concentration after about 18 hours, which corresponds to ca. 8.7×10^{-3} mol/L (90 % of the theoretical yield). Many studies have employed a reaction temperature over 60 °C for transesterification[41,42], but even at 30 °C, the conversion fraction reached 90 % although it took a somewhat longer

reaction time. The production rate could be seemed to be faster in the case of using $C_{RE\text{-}900}$ than that of $C_{SS\text{-}900}$. The reason for this fact could be considered that the mode diameter of $C_{RE\text{-}900}$ is smaller than that of $C_{SS\text{-}900}$, as shown in Figure 2, which suggested that the larger specific surface area of $C_{RE\text{-}900}$ affected the apparent production rate. Figure 5 shows the time course of methyl palmitate production in the case of using $C_{SS\text{-}900}$ and $C_{SS\text{-}1000}$. The dosage of both catalysts was 0.05 g and the initial concentration of tripalmitin was 3×10^{-3} mol/L. The experiments were conducted in a 30 °C water bath. The plots of the open and the solid circles are the same data shown in Figure 4. As seen in Figure 5, there was no significant difference in both data, in addition, there was also no significant difference in the time course of methyl palmitate production in the case using a $C_{SS\text{-}800}$ for 4 hours (data are not shown). It was reported that calcined shells from 800 to 1000 degrees could be recognized as CaO judging from the measurement of powder X-ray diffraction patterns[34,43]. This fact suggested that there was no difference in qualitative properties between $C_{SS\text{-}900}$ and $C_{SS\text{-}1000}$ as the catalyst.

Arai et al. (1981) pointed out that CaO could change into calcium methoxide by immersing CaO into methanol at room temperature for about five hours[42]. Some researchers have suggested that calcium methoxide acts essentially as a solid base catalyst under reaction conditions[43,44]. On the other hand, Kouzu et al. (2008) reported that calcium glyceroxide consisted of binding CaO and glycerol as a byproduct and calcium diglyceroxide will be the active phase with the catalytic reaction using CaO for transesterification[45]. Catarino et al. (2019) reported that calcium diglyceroxide (CaD) was used as the catalyst for biodiesel production through oil methanolysis and the catalytic activity of CaD was lower than that of CaO, which suggested that the CaD catalyst was more soluble than CaO[46]. The following is speculation, the reason why the faster reaction rate with $C_{RE\text{-}900}$ might be related to the difference in the degree of formation of methoxide and diglyceroxide on the $C_{RE\text{-}900}$ and $C_{SS\text{-}900}$ surfaces.

3.3. The relationship between active site number and the reaction rate constant

The performance of the catalyst would be assessed by the catalytic reaction rate which could be characterized using the overall reaction rate constant. Three moles of methyl palmitate are produced from one mole of tripalmitine stoichiometrically. Considering the stoichiometric relationship and the mass balance, the following equation is obtained as follows,

$$\frac{dC_{MP}}{dt} = k\left(C_{TPi} - \frac{1}{3} C_{MP} \right). \quad (1)$$

Where, C_{MP} and C_{TPi} represent the concentration of methyl palmitate at a time, t, and the initial concentration of tripalmitin, respectively. k represents the overall reaction rate constant. By solving Eq. (1) using the initial condition (C_{MP} = 0 at t =0), the following equation is obtained,

$$\ln\left(1 - \frac{C_{MP}}{3C_{TPi}} \right) = -\frac{1}{3} kt. \quad (2)$$

By plotting the left side of Eq. (2) versus t, a linear relationship through the origin could be obtained, and k could be determined from the slope of the regression line. Figure 6 shows the plot of Eq. (2) for the experimental data shown in Figure 4. Linear relationships were obtained although some scatters were observed. The solid lines in Figure 6 are the calculated lines using the determined k values.

The active basic sites of C_{RE} and C_{SS} were determined by titration with benzoic acid[37,38].

Xuejun et al. reported that the active sites on calcium oxide corresponded to the "O^{-}" and "Ca^{+}" on the surface[47-52]. The results were summarized in Table 2. Comparing with the number of the active sites of $C_{SS\text{-}900}$ and $C_{SS\text{-}1000}$, a significant difference was not observed. Comparing the amount of the active sites per unit mass of C_{RE} and C_{SS}, it seems to be affected by the origin of the raw materials (reagent or shell). However, comparing the number of the active sites per unit mass of CaO in C_{RE} and C_{SS}, it is considered that there is little difference between the raw materials of the catalysts (reagent or shell). The relationship between the number of the active sites and k determined from Eq. (2) is shown in Figure 7. As seen in the figure, a linear relationship was confirmed. The solid line is the regression line with the coefficient of determination, $R^2 = 0.89$. The value of the slope was 1.11×10^{4}. This relationship is very important to design and develop a transesterification reaction using C_{SS}. This result suggests that it is necessary to obtain the relationship between the number of active sites and k. The relationship is one of the most important factors in heterogeneous catalytic reactions rather than simply determining the optimal conditions for each experiment. We should verify that the relationship between the active sites based on CaO content and k is effective to predict the concentration of the product, methyl palmitate. The different initial tripalmitin concentrations, which were not involved to obtain the results shown in Figure 7, were employed and a verification experiment was conducted with $C_{SS\text{-}900}$. The results were shown in Figure 8. The initial concentrations of tripalmitin were 1.0 mmol/L (circle) and 5.0 mmol/L (triangle). The calculated curve agreed with the experimental values although some scatters were observed. In addition to the relationship shown in Figure 7, the average mass ratio of the calcined particle and the CaO content was 0.439, and the ratio of the number of active sites to the CaO content was 3.77×10^{-5} mol/g-CaO, which were obtained from the data shown in Table 2. The k value used in the calculation was 9.22×10^{-3} min^{-1}. The R^2 values were 0.78 (1.0 mmol/L) and 0.91 (5.0 mmol/L).

4 CONCLUSIONS

For the utilization of the calcined waste scallop shell as a heterogeneous basic solid catalyst for biodiesel production, the transesterification experiments were conducted with tripalmitin as a model triglyceride. Under the calcination condition at 900 °C or 1000 °C for 4 hours, the calcined scallop shell was sufficiently converted to calcium oxide (CaO), which was confirmed by measurement of the X-ray diffraction pattern. The transesterification reaction was conducted in a 30 °C water bath. Even in the relatively low temperature, ca. 90 % of the theoretical transesterification yield was obtained within 8-10 hours. On the calcined scallop shell, the difference in the calcination temperature was not affected by the overall reaction rate constant. In the case of using the calcined scallop shell, the overall reaction rate was lower than that in the case of using the calcined $CaCO_3$ (reagent), which was considered to be caused by the difference in CaO content. The active sites of the calcined catalysts were determined by titration with benzoin acid. As for the calcined scallop shell, the overall reaction rate constant, *k*, was proportional to the number of the active sites. In addition, by using the relationship between the mass content of CaO and the ratio of the number of the active sites to the mass of CaO, the time course of the yield of the product (methyl palmitate) could be estimated. We could verify this estimation method and show it is one of the strategies for biodiesel production using a calcined shell catalyst. In a further study, we would like to extend this strategy to the estimation of biodiesel production in a continuous operation.

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DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

NOTAION

C_{MP}	Concentration of methyl palmitate	[mol/m^3]
C_{TPi}	Initial concentration of tripalmitin	[mol/m^3]
k	overall reaction rate constant	[min^{-1}]
t	time	[min]

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Figures and tables captions

FIGURE 1 Scanning electron microscopy images of (A) raw CaO (reagent) particles, (B) $C_{RE\text{-}900}$, (C) $C_{RE\text{-}1000}$, (D) $C_{SS\text{-}0}$, (E) $C_{SS\text{-}900}$, and (F) $C_{SS\text{-}1000}$

FIGURE 2 Size distribution of (A) raw and calcined reagent (CaO) and (B) pulverized and calcined scallop shell particles

FIGURE 3 X-ray diffraction patterns of raw CaO (bottom) and calcined scallop shell particle (top). The pulverized scallop shell particle was calcined at 900 °C for 4 hours

FIGURE 4 Typical time course of production of methyl palmitate. The experiments were conducted with varying the mass of $C_{RE\text{-}900}$ and $C_{SS\text{-}900}$. The initial concentration of tripalmitin was 3.0×10^{-3} mol/L

FIGURE 5 Influence of calcination temperature on time course of production of methyl palmitate for $C_{RE\text{-}900}$, $C_{SS\text{-}900}$ and $C_{SS\text{-}1000}$. The initial concentration of tripalmitin was 3.0×10^{-3} mol/L

FIGURE 6 Fitting of the results shown in Figure 4 to Eq. (2) for determination of the overall reaction rate constant, k

FIGURE 7 Relationship between number of active sites existing the calcined particle surface and the overall reaction rate constant, k, determined from Eq. (2)

FIGURE 8 Comparison of the experimental value and the predicted value (solid lines) for the concentration, C_{MP}, of methyl palmitate by transesterification reaction using $C_{SS\text{-}900}$. The experimental condition of the initial tripalmitin concentration were 1.0×10^{-3} mol/L (open

circle) and 5.0×10^{-3} mol/L (open triangle). The dosage of $C_{SS\text{-}900}$ was 0.05 g

TABLE 1 Elemental composition and compounds content of the calcined particles

TABLE 2 Summary of calcination conditons, number of active sites, CaO content for calcined raw materials

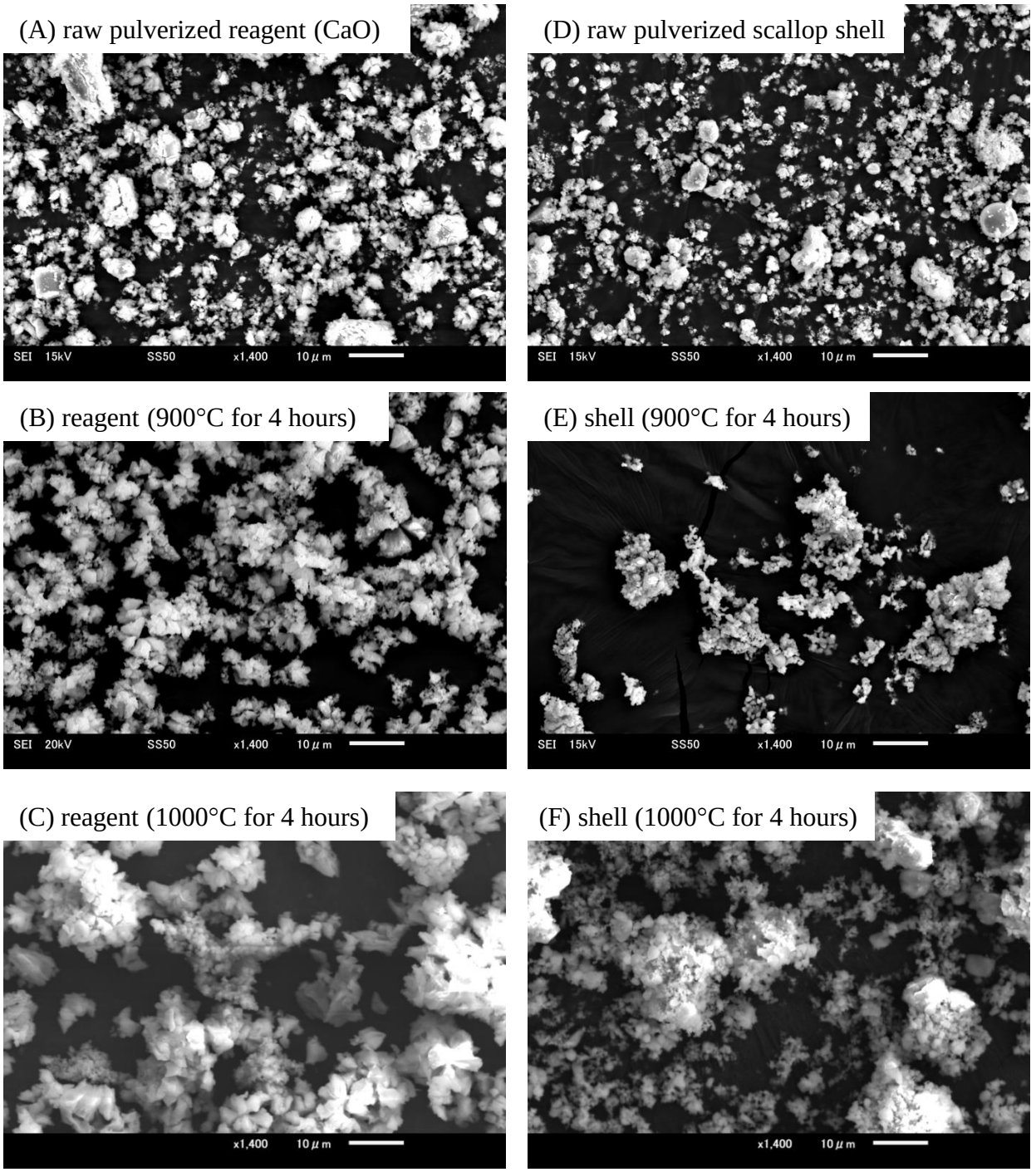


FIGURE 1 Scanning electron microscopy images of (A) raw CaO (reagent) particles, (B) $C_{\text{RE-900}}$, (C) $C_{\text{RE-1000}}$, (D) $C_{\text{SS-0}}$, (E) $C_{\text{SS-900}}$, and (F) $C_{\text{SS-1000}}$

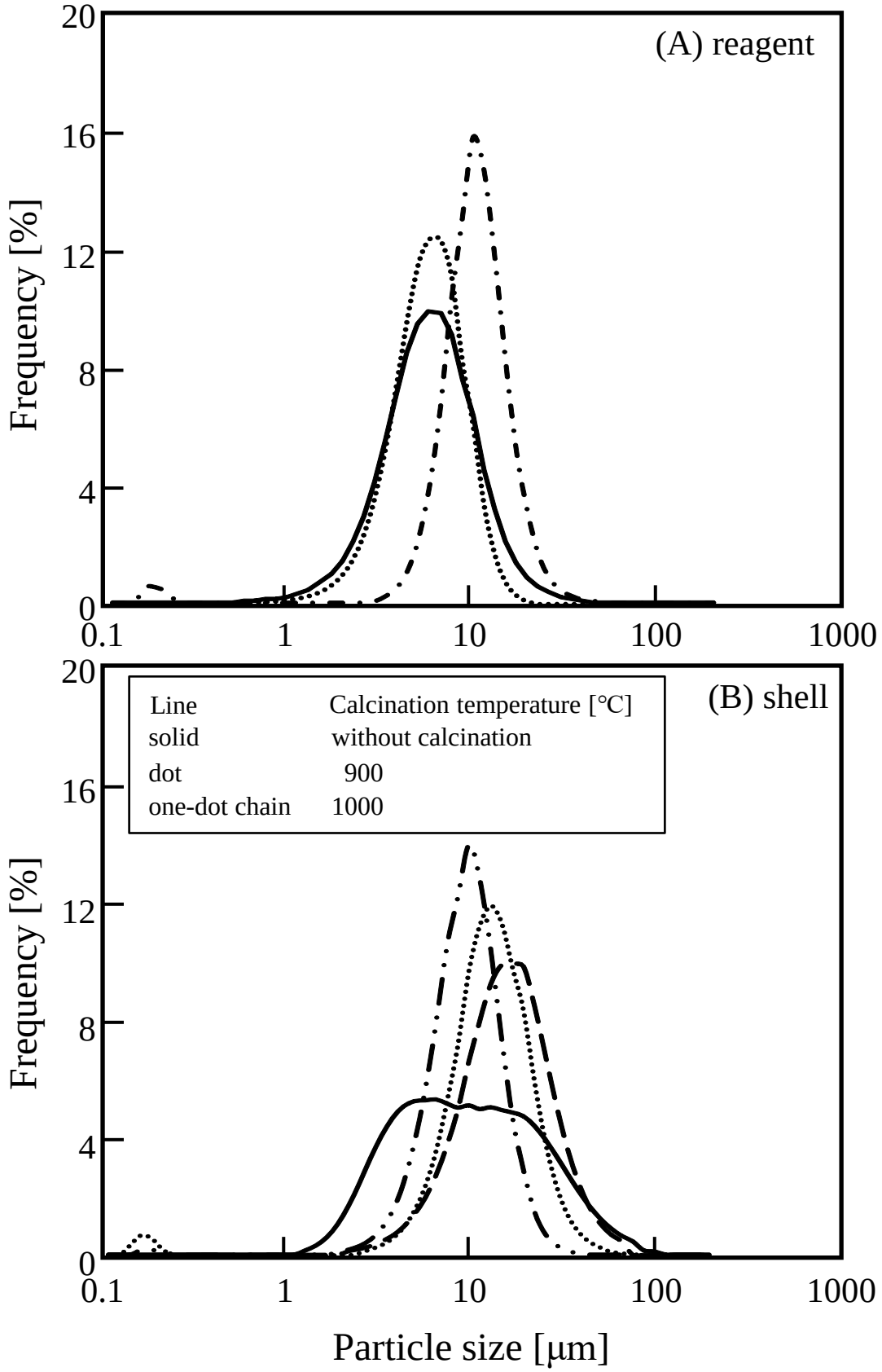


FIGURE 2 Size distribution of (A) raw and calcined reagent (CaO) and (B) pulverized and calcined scallop shell particles

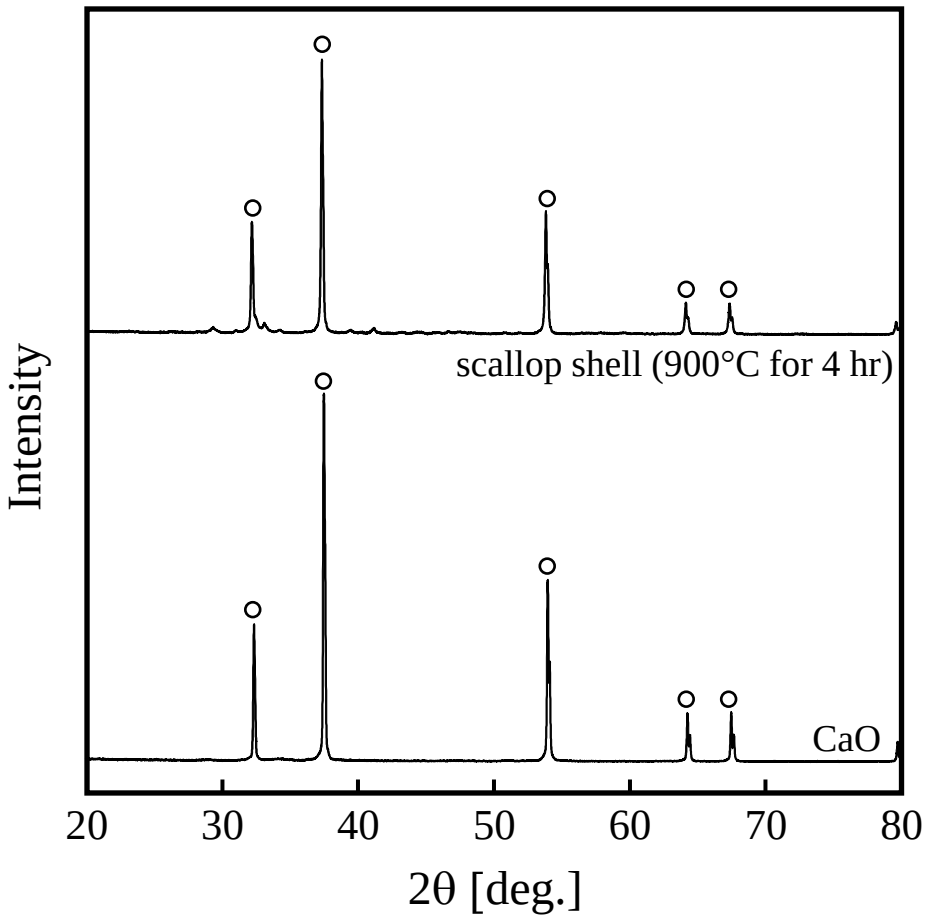


FIGURE 3 X-ray diffraction patterns of raw CaO (bottom) and calcined scallop shell particle (top). The pulverized scallop shell particle was calcined at 900 °C for 4 hours

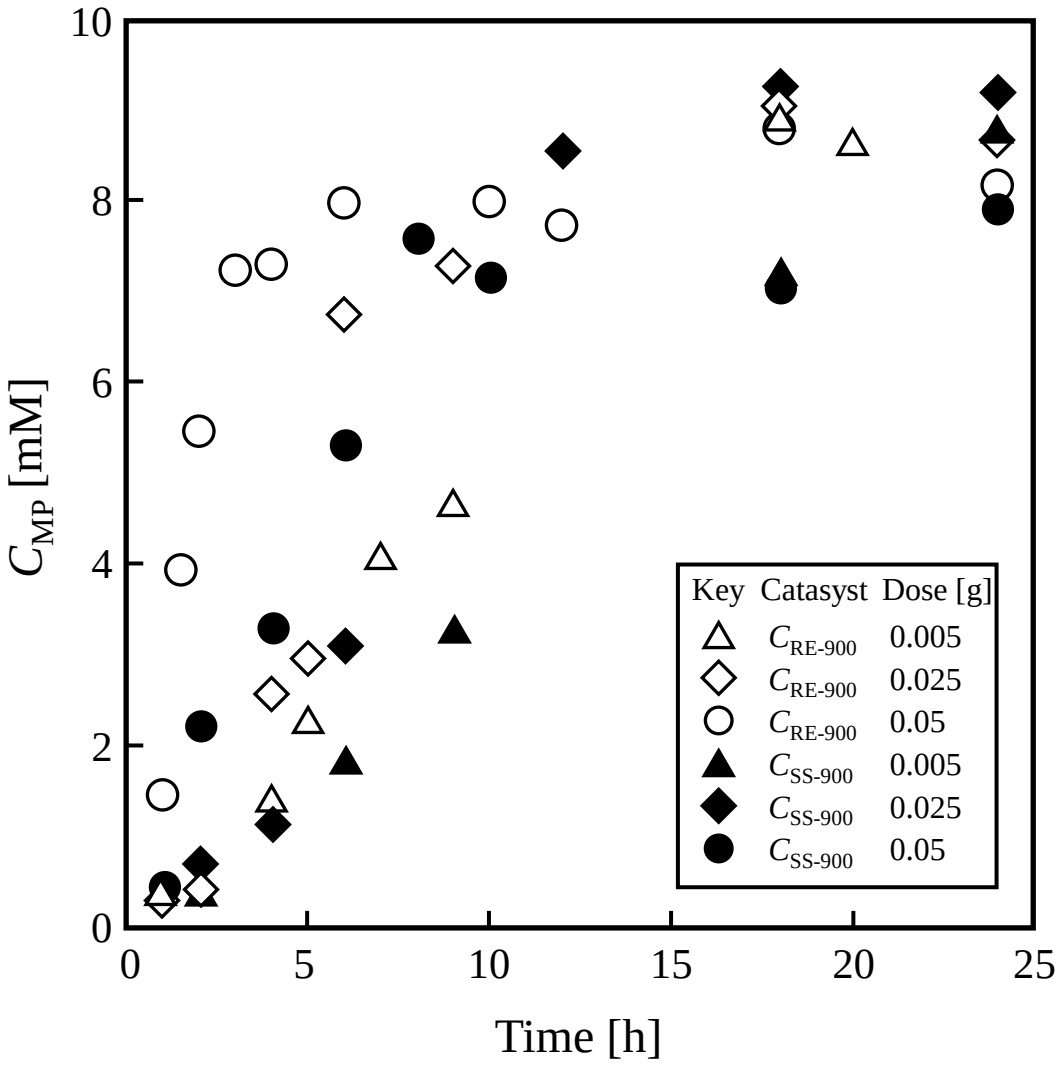


FIGURE 4 Typical time course of production of methyl palmitate. The experiments were conducted with varying the mass of C_{RE-900} and C_{SS-900}. The initial concentration of tripalmitin was 3.0×10^{-3} mol/L

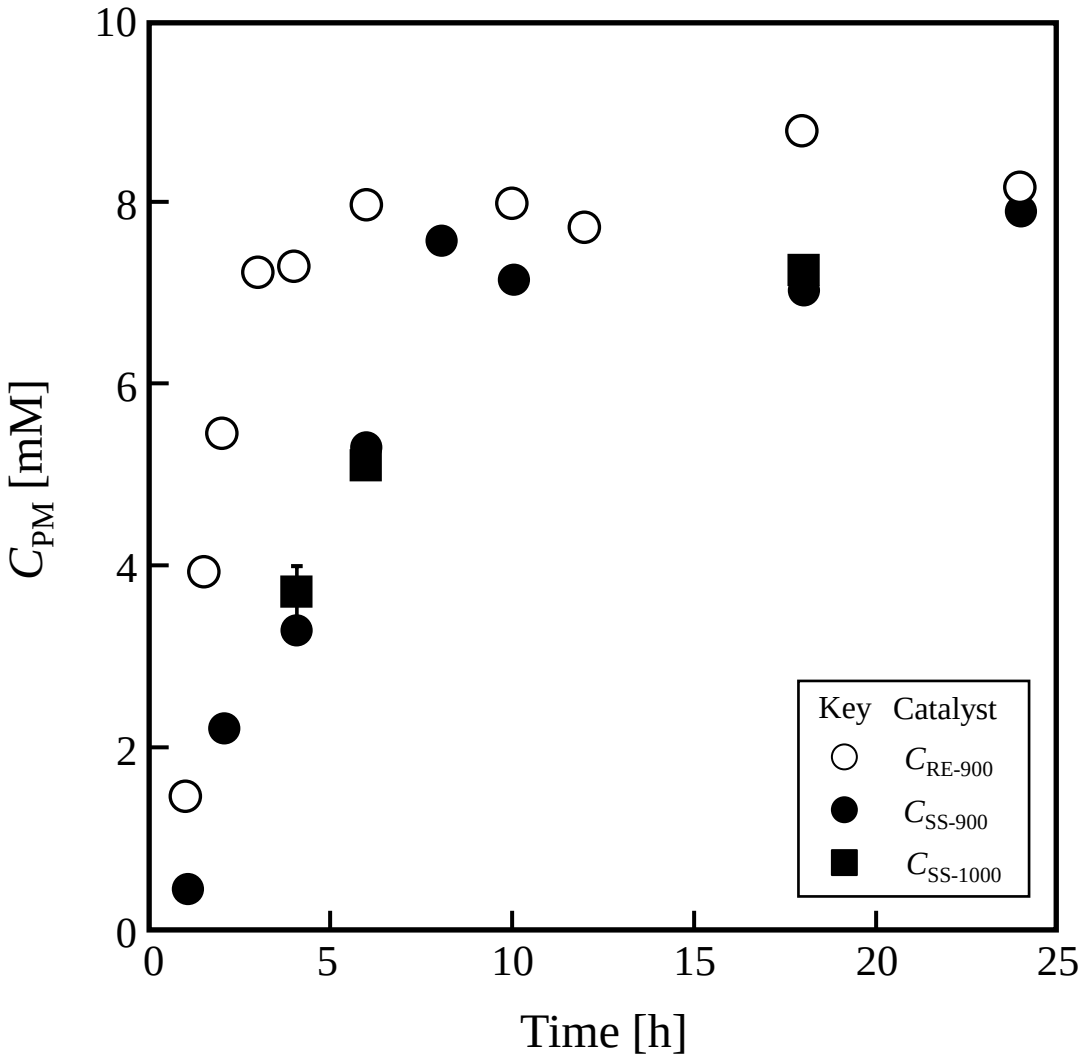


FIGURE 5 Influence of calcination temperature on time course of production of methyl palmitate for C_{RE-900}, C_{SS-900} and $C_{SS-1000}$. The initial concentration of tripalmitin was 3.0×10^{-3} mol/L

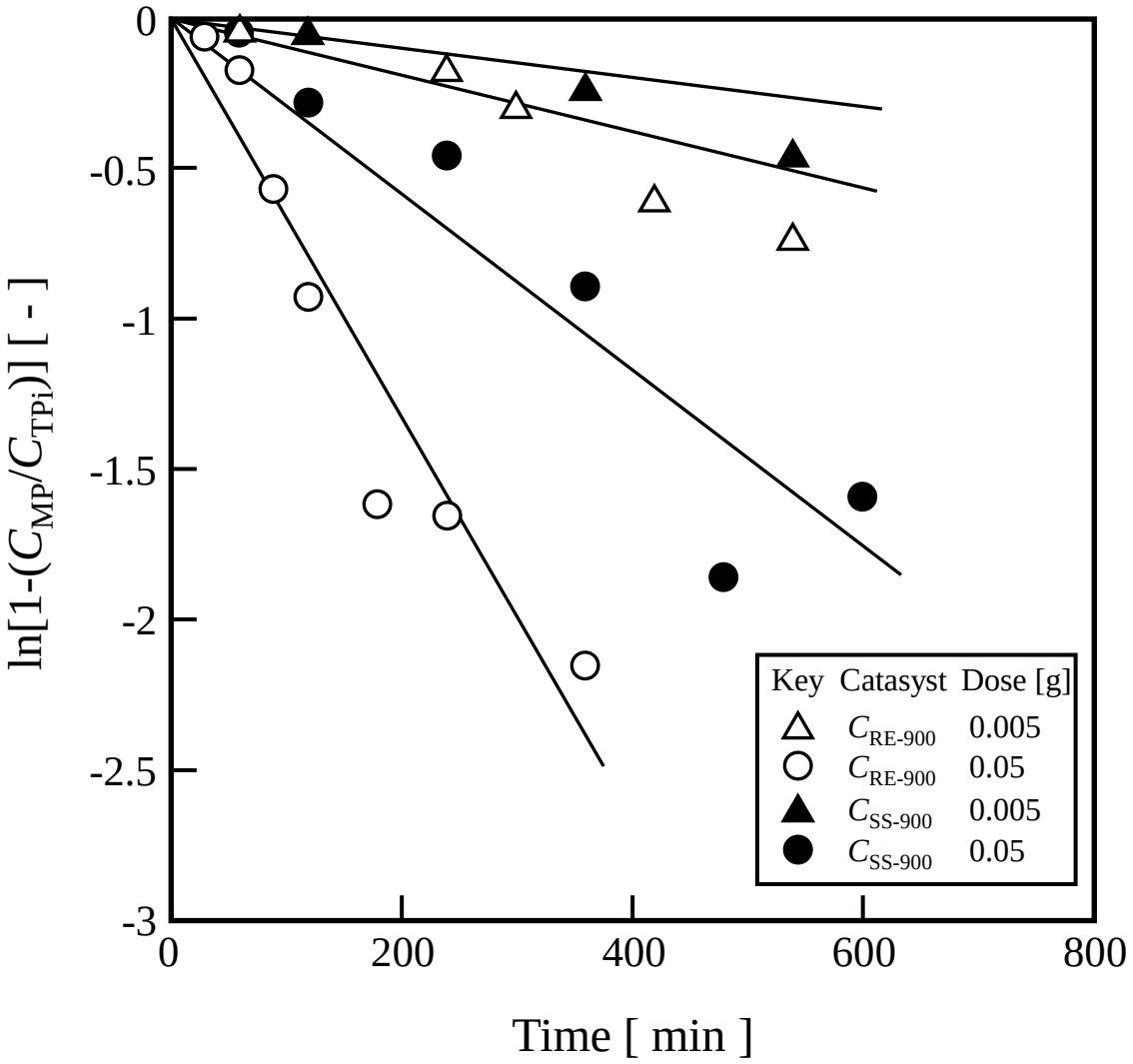


FIGURE 6 Fitting of the results shown in Figure 4 to Equation (2) for determination of the overall reaction rate constant, *k*

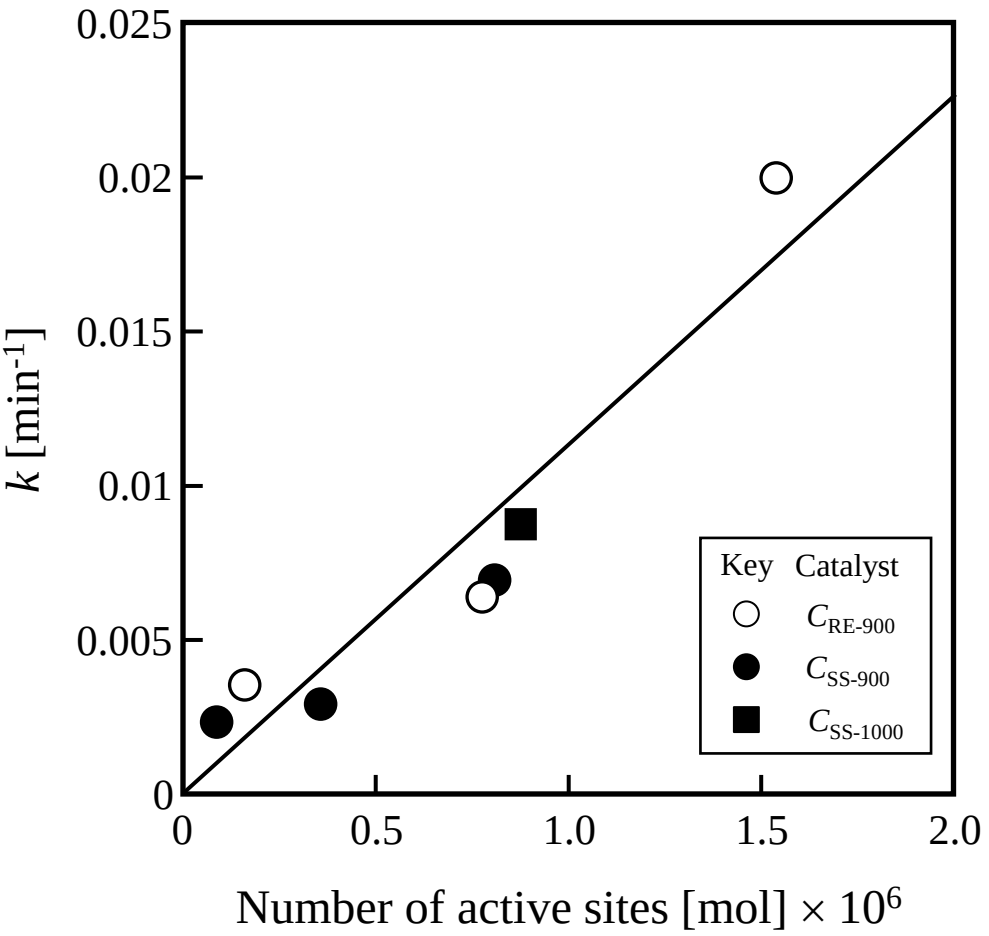


FIGURE 7 Relationship between number of active sites existing the calcined particle surface and the overall reaction rate constant, k, determined from Equation (2)

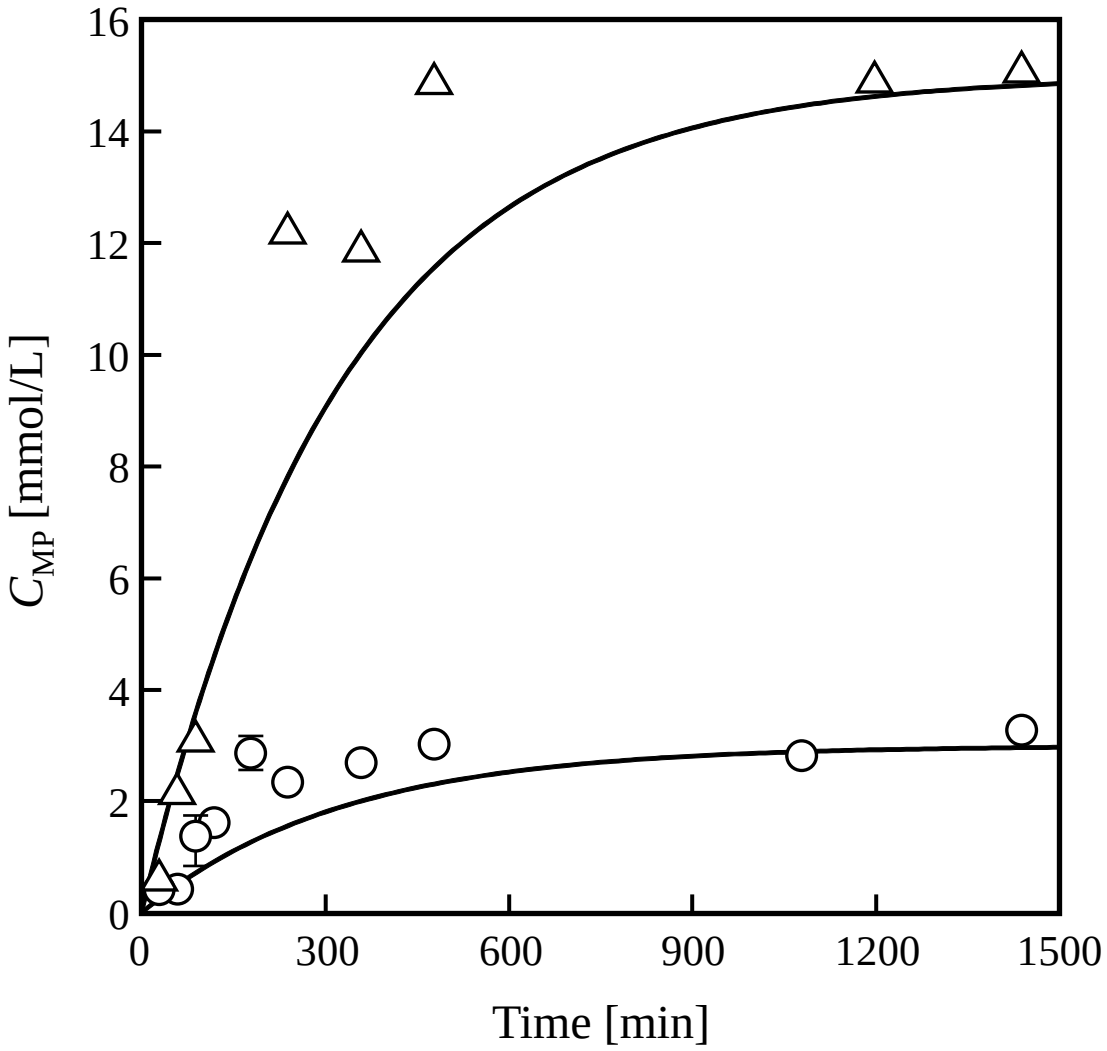


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TABLE 1 Elemental composition and compounds content of the calcined particles

material	temperature [℃]	element [mol%]			catalyst [mol%]	
		C	O	Ca	CaO	$CaCO_3$
reagent	900	11.6±1.4	49.3±10.5	38.8±9.4	68.5±2.4	31.5±2.4
	1000	10.7	55.5	32.9	66.9	33.1
shell	900	14.2±1.5	61.2±4.5	24.6±3.0	41.1±5.7	58.9±5.7
	1000	17.1	41.9	34.0	43.4	56.6

TABLE 2 Summary of calcination conditons, number of active sites, CaO content for calcined raw materials

material	calcination condition	dosage [g]	Active site [μmol/g]	CaO [mol%]	Active site [μmol/g-CaO]
$CaCO_3$ (reagent)	900°C, 4 h	0.0051	32.2	71	45.4
		0.0250	31.1	68	45.7
		0.0501	30.8	71	43.4
shell	900°C, 4 h	0.0051	17.8	41	43.4
		0.0250	14.3	36	39.7
		0.0501	17.6	47	37.5
	1000°C, 4 h	0.0499	16.2	43	37.4