1. Introduction

The depletion of recoverable fossil fuels, global warming caused by climate change, and the unstable price of fossil fuels have motivated us to find alternative fuels derived from renewable resources. The agreement to achieve global energy-related greenhouse gas (GHG) emissions in 2050 of 50% below the 1990 or current level was signed at the G8 L’Aquila Summit, accelerating the development of alternative fuels.

According to the roadmaps proposed by the International Energy Agency (IEA)¹, liquid and gaseous fuels derived from organic matter will make a major contribution to reducing energy-related GHG emissions (including CO₂) in the transport sector and promoting energy security. The IEA claim that biofuels produced by new technologies could provide 27% of total transport fuel, in particular diesel, kerosene, and jet fuels by 2050, whereas biofuels currently account for only 3% of total transport fuel. To realize this vision, conventional biofuel technologies, such as biomass to liquid, cellulosic ethanol production, algae-based biodiesel production, and hydrodeoxygenation of oils and fats, require further research and development, and the demonstration of commercial-scale plants to ensure these technologies reach maturity¹. Therefore, the scenario based on the roadmaps reported by the IEA suggests that conventional techniques will be the main routes for producing biofuels until 2030, whereas the advanced technologies, once commercially proven, will help reach the biofuel demand set in the roadmaps beyond 2030. It is worth noting that government support, international collaboration, and biomass and biofuel trade are also needed to realize the scenario¹. Among the conventional technologies, our research group has focused on biodiesel fuel (BDF) production from edible oils (rapeseed oil, sunflower oil, sesame oil, etc.), non-edible oils (jatropha oil, etc.), waste cooking oils, and animal fats because this technique has problems with conversion efficiency, the operation procedure, and the dissolution of the active phases during the process.

BDF, which has fatty acid methyl esters (FAME) as its main component, has attracted attention as an alternative to petroleum diesel fuel because FAME is carbon-neutral and renewable, has no aromatic hydrocarbons and low sulfur content, and is non-toxic²⁻⁴. Although edible oils, non-edible oils, animal fats, and waste cooking oil are used as feedstock for producing BDF, only waste cooking oil can be a feedstock in...
Japan owing to the limited number of routes for collecting oils. A specific catalyst is normally required for BDF production\(^{25}\)–\(^{27}\), and the advantages and disadvantages of different catalyst systems are summarized in Table 1\(^{10}\)–\(^{13}\). Although homogeneous base catalysts, such as sodium and potassium hydroxides, show high activity for the process under mild reaction conditions, there are several drawbacks, including soap formation, complex purification steps, and the formation of a large amount of wastewater, especially in the presence of water and free fatty acids derived from the feedstock\(^{10}\)–\(^{12}\). In contrast, the homogeneous acid catalyst tolerates water and free fatty acids, allowing simultaneous esterification and transesterification; however, corrosion occurs inside the reactor and pipeline and purification steps are necessary to separate the catalyst from the products\(^{10}\)–\(^{12}\). Considering the properties of the homogeneous catalysts, waste cooking oil, which contains water, free fatty acids, and triglyceride, is recycled for BDF by water removal, free fatty acid esterification with an acid catalyst, and the transesterification of triglycerides with base catalyst\(^{17}\)–\(^{19}\). However, separating homogeneous catalysts from the products requires expensive, complex purification steps that create lots of wastewater. These problems have been addressed by the development of various heterogeneous catalysts that can be separated easily from the products by filtration, minimizing the generation of wastewater\(^{10}\)–\(^{12}\). Although the heterogeneous catalysts have a reaction rate that is higher than the rate of the enzymatic reaction, the catalytic activity is low compared with the homogeneous catalysts, and catalyst leaching must be overcome to commercialize heterogeneous catalysts\(^{10},17,20\)–\(^{36}\).

Table 1 Advantages and Disadvantages of Different Catalyst Systems\(^{10}\)–\(^{13}\)

| Catalyst system        | Advantages                                      | Disadvantages                  |
|------------------------|-------------------------------------------------|--------------------------------|
| Homogeneous base catalyst | High activity                                 | Soap formation                 |
|                        | Cheap                                           | Purification needed            |
|                        | No corrosion                                    | Wastewater                     |
| Homogeneous acid catalyst | Tolerance toward water and free fatty acids | Corrosion                      |
|                        | Simultaneous esterification and transesterification possible | Purification needed            |
|                        |                                                  | Wastewater                     |
| Heterogeneous base catalyst | Easy separation                               | Active phase leaching          |
|                        | Catalyst reusable                               | Catalyst cost                  |
|                        | No corrosion                                    | Diffusion limitation           |
| Heterogeneous acid catalyst | Easy separation                               | Catalyst leaching              |
|                        | Catalyst reusable                               | Catalyst cost                  |
|                        | Free fatty acid is converted.                   | Diffusion limitation           |
|                        |                                                  | Harsh reaction conditions       |
| Enzyme                 | Low energy use                                  | Slow reaction rate             |
|                        | Fewer purification steps                        | High enzyme cost               |
|                        |                                                  | Deactivation by alcohol and byproducts |

We have focused on calcium oxide (CaO) as a heterogeneous base catalyst for the transesterification of oils because this catalyst has a high activity and stability among alkaline earth oxide catalysts (CaO, SrO, BaO, MgO), and has a smaller environmental impact than homogeneous base catalysts\(^{10},13,14,17\). However, CaO has lower catalytic activity than homogeneous catalysts, especially when the catalyst is poisoned by ambient CO\(_2\) and H\(_2\)O\(^23\), and calcium leaches from the catalyst during the reaction\(^{17,20}\)–\(^{36}\). The catalytic activity could be increased by appropriate pretreatment of the catalyst before the reaction\(^{23,37,38}\). To prevent leaching, catalyst stability has been improved by preparing supported CaO, such as CaO/ZnO, CaO/mesoporous silica, and CaO/MgO catalysts\(^{10,13,14,28,29,31,32}\), or by forming binary mixed oxide catalysts\(^{10,14,35}\). Even though calcium leaching from the catalyst surface occurred during the reaction, leached Ca species could be removed from the products by ion-exchange resin\(^{39}\). Alternative approaches to improving the catalytic performance of heterogeneous catalysts have been proposed by other research groups. They have attempted to create a suitable environment around the catalyst by microwave irradiation\(^{40,41}\), ultrasonic irradiation\(^{42,43}\), supercritical solvent\(^{44}\), and the addition of co-solvent\(^{45,47}\). However, microcapsules also provide a reaction field to create a suitable environment for catalytic reactions including enzymatic reactions, photosynthesis, and organic synthesis\(^{48,49}\). Therefore, we used capsules as a reaction field for rapeseed oil methanolysis with the CaO catalyst, and the catalytic performance of CaO powder, CaO-loaded capsules, Ca(OH)\(_2\) powder, KOH as a homogeneous catalyst, and the capsules themselves were compared\(^{50}\). Figure 1 shows the BDF yield obtained with different catalyst systems (same total catalyst loading amount of 0.5 wt% based on the amount...
of rapeseed oil in the reaction mixture) at a reaction temperature of 333 K with a stirring rate of 150 rpm for certain reaction times. The CaO-loaded capsule showed activity, whereas the capsule produced no yield, indicating that the encapsulated CaO catalyst is the active phase for rapeseed oil methanolysis. Surprisingly, the reaction rate of the CaO-loaded capsule system was faster than that of the CaO and Ca(OH)$_2$ powder catalysts. This result suggested that special pretreatment is not necessary to activate the CaO catalyst loaded in the capsule and the reactant and product permeation rates through the capsule shell did not have a detrimental effect on the reaction rate of BDF synthesis. Although the CaO-loaded alginate capsule system showed a lower catalytic activity than the homogeneous catalyst (KOH) did, we concluded that this is a promising catalyst system for rapeseed oil transesterification with methanol. In addition, a detailed study on process parameters was performed with this catalyst system, and the reaction conditions where this catalyst system showed the best performance were identified. Encapsulating the CaO catalyst in the capsule system prevented the Ca species leaching and CaO-loaded alginate capsules showed the same activity for three consecutive runs of the BDF synthesis$^{50}$. Therefore, in this review paper, first, we show the reaction mechanism for CaO-loaded alginate capsules, and then we explain why this catalyst system showed a higher activity than the CaO powder catalyst. In addition, our research group has been investigating tools, such as mantle heaters, water baths, and oil baths, which are usually used to keep the reactor at the desired reaction temperature. However, much energy is consumed by convection methods during BDF synthesis reactions to reach and maintain the reaction temperature. Thus, we proposed a new heating method to achieve the desired temperature inside the capsule, while the temperature of the reaction mixture is lower$^{49}$. In our method, a photothermal exchange material, which converts light energy to heat energy, is also encapsulated in the capsule. Operating the system precisely allows selective heating in the capsule because light penetrates the capsule shell. Consequently, the energy required to reach and maintain the reaction temperature could be saved. In this review paper, we prepared amorphous N-doped TiO$_2$ powder$^{52}$ and TiO$_2$-supported Cr$_2$O$_3$ powder$^{53}$ as photothermal exchange materials combined with commercial active carbon powder$^{51,54}$. The samples were loaded inside the capsule with CaO catalyst and various capsules were prepared. These capsules were used for rapeseed oil methanolysis under light irradiation to compare the catalytic performance with various capsule systems. In addition, we discuss the effect of the irradiation power on the BDF yield obtained with the capsule systems.

2. Experimental

2.1. Materials

CaO powder with a BET surface area of 7 m$^2$ g$^{-1}$ was purchased from Wako Pure Chemical Industries, Ltd. and was used as a catalyst with no purification or treatment$^{51-55}$. The X-ray diffraction (XRD) pattern showed a CaO phase with minor CaCO$_3$ and Ca(OH)$_2$ phases. Sodium alginate and CaCl$_2$ were purchased from Kanto Chemical Co., Inc. and were used for preparing the capsules. Titanium tetraisopropoxide (TTIP; Ti(OCH(CH$_3$)$_2$)$_4$; $>97.0\%$, Kanto Chemical), hydrazine dihydrochloride (N$_2$H$_6$Cl$_2$; $>98.0\%$, Kanto Chemical), dry 2-propanol (IPA; $>99.7\%$, Kanto Chemical), and 50% hydroxyamine aqueous solution (Wako Pure Chemical Industries) were used to prepare an amorphous N-doped titanium oxide powder that was used as a photothermal exchange material in the BDF synthesis reaction. Cr(NO$_3$)$_3$·9H$_2$O (Kanto Chemical) and TiO$_2$ powder (P25, Evonik Ind.) were used to prepare TiO$_2$-supported Cr$_2$O$_3$ as another photothermal exchange material. An active carbon powder (Kanto Chemical) was also used as a photothermal exchange material. Methanol (Kanto Chemical), rapeseed oil (Nacalai Tesque Inc.), and tetraydrofuran (THF, Kanto Chemical) were used for BDF synthesis. The rapeseed oil consists of 2% stearic acid, 4.3% palmitic acid, 9.5% linolenic acid, 20.5% linoleic acid, 60.6% oleic acid, and trace amounts of other acids. Details of the rapeseed oil have been reported previously$^{50}$. Methyl heptadecanoate (Tokyo Chemical Ind. Co., Ltd.) and hexane (Kanto Chemical) were used for preparing the samples for gas chromatography–flame ionization
2.2. Photothermal Exchange Material Preparation

Amorphous N-doped TiO$_2$ powder was prepared by the sol-gel method at low temperature with the specified catalyst as follows.$^{52,56}$ TTIP (4.26 g) was dissolved in dry IPA (10.59 g) under a nitrogen gas atmosphere to prepare the TiO$_2$ precursor solution. The catalyst solution was an aqueous solution of 0.74 mol L$^\text{-1}$ hydrazine dihydrochloride (0.44 g) dissolved in dry IPA (9.05 g) under ultrasonic irradiation. The TiO$_2$ precursor solution was slowly added to the catalyst solution under stirring at 1500 rpm. The mixture was placed in a tightly sealed bottle and kept at 298 K under continuous stirring for 4 days. After that, 2.5 wt% hydroxylamine aqueous/dry IPA solution was added as a nitrogen dopant, controlling the amount added corresponding to N/Ti molar ratios of 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5, and then the mixture was stirred at 298 K in an oven for 1 day. Amorphous N-doped TiO$_2$ powders with different N/Ti molar ratios were obtained after the solvent was completely evaporated. In some cases, the powders were further hydrated in distilled water at 313 K for 12 h with a stirring rate of 1500 rpm to hydrolyze residual organic species and allow the condensation of hydroxyl groups. This sample is denoted as an N-doped TiO$_2$ powder (treated).

Cr$_2$O$_3$ supported on TiO$_2$ was prepared by the conventional impregnation method.$^{57-59}$ TiO$_2$ powder (P25, 10 g) was added to aqueous Cr(NO$_3$)$_3$·9H$_2$O solution with various Cr concentrations (5, 10, 18, 30 wt%) corresponding to the apparent Cr loading of the photothermal exchange material. The mixture was stirred at 350 rpm and 383 K until the solvent was evaporated completely. The powder was dried at 383 K for 12 h and calcined in air at 773 K for 6 h.

2.3. Characterization of the Photothermal Exchange Materials

Because photothermal exchange materials must be insoluble in the reactants for BDF synthesis (rapeseed oil, methanol, and THF), a solubility test was conducted on the samples. The sample (50 mg) was added to the reactants and stirred for 1 h, and then the mixture was left overnight to check the solubility of the sample in the reactants.

XRD measurements of the photothermal exchange materials were carried out with an X-ray powder diffractometer (RINT-2100, Rigaku Corp.) with Cu Kα radiation (tube current, 40 mA; tube voltage, 40 kV)$^{52,53}$). The XRD patterns were measured in a 2θ range 2-80$^\text{o}$ at a scanning speed of 2° min$^{-1}$. The sample morphology was determined by scanning electron microscopy (SEM; S-4500, Hitachi, Ltd.), and energy dispersive X-ray spectroscopy (EDX; EMAX-5770, HORIBA, Ltd.) was used to evaluate the elemental composition.$^{53}$

The chemical compositions of the samples were determined by X-ray fluorescence spectroscopy (XRF; SEA2100 L, SII Nanotechnology Inc.$^{53}$). The UV-Vis spectra of the samples were recorded by using a diffuse reflectance UV-Vis spectrometer (V-660, JASCO Corp.) with an integrating sphere and BaSO$_4$ as the reference.$^{52,53}$ The Fourier transform infrared spectroscopy (FT-IR) spectrum of the active carbon powder in a KBr pellet was obtained in transmission mode (FT/IR-4200 type A, JASCO) with 16 scans in the range of 4000-650 cm$^{-1}$ at a 1 cm$^{-1}$ resolution$^{51,54}$. To estimate the photothermal exchange properties of the samples, the temperature of the reactants and the sample was measured under light irradiation using a xenon lamp (150WGS, Hamamatsu Photonics K.K.; power 150 W, current 8.5 A) with a condenser lens (SLSQ-40-150P, Sigma Koki Co., Ltd.$^{52,54}$). The reactants (5 mL; rapeseed oil : methanol : THF = 20 : 10 : 13) and various amounts (0-30 mg) of the samples were placed in the test tube. The mixture (sample concentration, 0-6 mg mL$^{-1}$) was stirred and irradiated with a xenon lamp, and a thermocouple was used to monitor the temperature.

Acetic acid oxidation was used to evaluate the photocatalytic activities of the samples.$^{21,53}$ Initially, 5 wt% aqueous acetic acid solution (2 mL) and the sample (20 mg) were placed in a quartz glass cell (11 cm$^2$). The solution was stirred at 900 rpm while the gas phase was purged with O$_2$ for 30 min. The cell was capped tightly, and the acetic acid solution was irradiated for 6 h with visible and UV light from a xenon lamp fitted with a filter. The gas phase was sampled with a syringe at 1 h intervals and analyzed by GC (GC2014, Shimadzu Corp.) with a Porapak Q column (GL Sciences Inc.) and a thermal conductivity detector to estimate the concentration of CO$_2$ generated. The results were used to calculate the conversion of acetic acid to CO$_2$.

2.4. Capsule Preparation

For the CaO-loaded capsules, the co-extrusion method using a coaxial needle with concentric nozzles was used to encapsulate CaO powder in an alginate shell.$^{50-55}$ A 10 wt% or 20 wt% suspension of commercial CaO in rapeseed oil (100 mg/g-oil or 200 mg/g-oil) and a 2 % (w/v) aqueous sodium alginate solution were supplied by syringe pumps (Model-100, Neuroscience) through the inner and outer nozzles at flow rates of 7.5 mL h$^{-1}$ and 50 mL h$^{-1}$, respectively. The two-phase droplets were collected in 0.4 M CaCl$_2$ solution and stirred at 300 rpm for 30 min to produce spherical capsules with a CaO-rapeseed oil core and a calcium alginate shell in a one-step gelling technique. The recovered capsules were washed thoroughly with distilled water. Lastly, the capsules were dried in an oven at 323 K for 10 h to obtain the CaO-loaded alginate capsules that were used for BDF synthesis with convection heating.
The capsules loaded with CaO and photothermal exchange material were prepared by a similar procedure to that described above. A typical preparation procedure using TiO2-supported Cr2O3 is described as an example. A suspension of commercial CaO and Cr2O3/TiO2 powder in rapeseed oil and a 2 % (w/v) aqueous alginate solution were supplied through the inner and outer nozzles by syringe pumps at the same flow rates as in the previous procedure. The two-phase droplets were collected in a 0.4 M CaCl2 solution and stirred at 300 rpm for 30 min. The recovered capsules were washed with distilled water and dried at 323 K in an oven for 10 h. Although the CaO concentration was fixed as 100 mg/g-oil, the concentration of CaO (100 mg/g-oil)-amorphous N-doped TiO2 (3.0 mg/g-oil)-loaded, and CaO (100 mg/g-oil)-active carbon (0.1 mg/g-oil or 2.0 mg/g-oil)-loaded alginate capsules were used for these tests as follows52–54). The capsules and the reactants (rapeseed oil, methanol, and THF: 1 mL) were placed in the micro cell. The micro cell was set up for light irradiation and the thermograph lens was focused on the top layer of capsules. After the samples were adjusted, data acquisition was started and light irradiation began after 5 s. Software analyzed the raw data and converted it to a JPEG file. The irradiation was over the full wavelength range (irradiation power, 3.6 W).

2.7. BDF Synthesis Using Mantle Heater

Rapeseed oil was transesterified in a batch reactor with methanol using CaO-loaded capsules and CaO-loaded capsules modified with silane coupling agents55. Rapeseed oil (20 mL) and capsules (0.48 g; total CaO loading 0.096 g) were placed in a spinner flask (50 mL) and sealed with a cap. A mantle heater was used to heat the rapeseed oil to 333 K with stirring at 300 rpm. The reaction was started at 333 K by adding methanol (10 mL; methanol/oil molar ratio, 12) to the mixture. At 1 h intervals, the reaction mixture was sampled (1 mL) and the sample was centrifuged (CR15RX, Hitachi) at 5000 rpm for 10 min. The supernatant was dried at 323 K for 2 h under vacuum, and the sample containing FAME was mixed with 0.05 % (w/v) methyl heptadecanoate/hexane solution (1 mL). The mixture (0.2 μL) was analyzed by GC-FID (GC-4000, GL Sciences; InertCap Pure-WAX column, GL Sciences, i.d. 0.53 mm, length 30 m, thickness 1.0 μm). Initially, the oven was at 423 K for 5 min, heated to 493 K at a rate of 5 K min⁻¹, and kept at 493 K for 15 min. The injector and detector temperatures were maintained at 523 K. The BDF yield based on the rapeseed oil weight was calculated by Eq. (1).

\[
\text{BDF yield [%]} = \frac{\sum A_{ES}}{A_{ES}} \times \frac{m_{ES}}{m} \times 100
\]

Here, \(\sum A_{ES}\) is the sum of the GC-FID peak areas of the five fatty acid methyl esters, \(A_{ES}\) is the GC-FID peak area of methyl heptadecanoate (external standard), \(m\) is the amount of unknown sample injected into the GC-FID, and \(m_{ES}\) is the amount of methyl heptadecanoate injected into the GC-FID.

2.8. Analysis of Liquid Phases Inside and Outside the Capsules

GC-FID was used to analyze the liquid phases collected from inside and outside the capsules at regular intervals during rapeseed oil methanolysis to measure the mass transfer of reactants and products, and to clarify the BDF synthesis mechanism55. During a typical BDF synthesis procedure, the reaction mixture was sampled at 1 h intervals over the reaction time of 6 h. After the capsules were removed from the liquid, the liquid was weighed and oven-dried at 323 K for 2 h.
under vacuum. The liquid was weighed after drying, and the weight difference before and after drying was ascribed to the loss of methanol from the reaction mixture. The remaining liquid, which contained FAME, unreacted triglyceride, and other products, was mixed with 0.05 % (w/v) methyl heptadecanoate/hexane solution. GC-FID (GC-4000, GL Sciences, DB-HT-SIMDIS column, Agilent Technologies, i.d. 0.53 mm, length 5 m, thickness 0.15 μm) was used to analyze the mixture (0.2 μL). The oven was initially at 373 K, heated to 423 K at a rate of 5 K min⁻¹, heated to 633 K at a rate of 10 K min⁻¹, and kept at 633 K for 2 min. The injector and detector temperatures were 653 K. The peak positions and concentration coefficients of FAME (Supelco FAME mix 18916-1AMP, Sigma Aldrich), triolein, 1,3-diolein, and monoolein were calculated before the unknown samples were analyzed. Based on the standard solution, the concentration (mol/L) of each product was calculated.

The recovered capsules were wiped gently with paper, placed inside the micro tube, and crushed. The tube was centrifuged (CF15RX, Hitachi) three times at 8000 rpm for 20 min to separate the liquid and solid phases. The liquid phase was transferred to another weighed micro tube and dried in an oven at 323 K for 2 h under vacuum. The residual liquid was weighed to calculate the amount of methanol in the capsules. To remove ions, such as Ca²⁺ and Na⁺, the liquid was purified with cation-exchange resin (Amberlyst-15 DRY, Sigma Aldrich) following a published method¹⁷. The GC-FID method above was used to analyze the purified liquid. The solids obtained after centrifugation were used for XRD analysis.

Similar experiments were also conducted for the reaction medium (outside the capsules) at 308 K with CaO-loaded active carbon-loaded capsules, using a xenon lamp instead of a mantle heater to achieve the desired reaction temperature.

2.9. BDF Synthesis under Light Irradiation²¹⁻⁵⁴

A xenon lamp unit (150WGS, Hamamatsu Photonics) was placed 20 cm from the reaction vessel containing the reactants and capsules, and a condenser lens (SLSQ-40-150P, Sigma Koki) was placed between the lamp and the vessel. We refer to irradiation with a condenser lens as condensed light irradiation here. In some experiments, to select the type of light with which the reaction medium was irradiated, five filters (CLDF-50S, SCF-50S-39 L, 1TF-50S-761R, GRF-50S-530G, UTVAF-33U, Sigma Koki) were used. In a preliminary test, the power of the light that reached the reaction medium was measured using a laser power meter (POWERMAX 5200, Molelectron Detector Inc.). For irradiation with the full wavelength range, infrared (IR) range, IR range with a slit, and the IR range with a slit and mesh the irradiation powers were 3.6, 2.1, 1.1, and 0.6 W, respectively. During BDF synthesis, the reactants and capsules were mixed with a magnetic stirrer. The reactant temperature was kept below 308 K by a temperature controller connected to a thermocouple and a fan. Rapeseed oil (20 mL), methanol (10 mL; methanol/oil molar ratio, 12), and capsules (0.96 g; total CaO loading: 0.096 g) in THF (1.3 mL) were placed in a 50 mL bottle and sealed with a silicone cap. To improve the affinity between rapeseed oil and methanol, THF was used as a co-solvent to form a single phase⁴⁵,⁴⁶,⁵¹⁻⁵⁴, greatly increasing the transparency of the reactant mixture and allowing light to penetrate the capsules. The solution was stirred at 300 rpm with no light irradiation, and then irradiated for the reaction time. Every 1 h, the reaction mixture was sampled (2 mL) and the liquid sample was centrifuged (CF15RX, Hitachi) at 5960 rpm for 10 min. The supernatant was dried at 323 K for 2 h under vacuum, and 0.05 % (w/v) methyl heptadecanoate/hexane solution (1 mL) was added to the samples containing FAME. An aliquot of the mixture (0.2 μL) was analyzed by GC-FID (GC-4000, GL Sciences, DB-HT-SIMDIS column, Agilent Technologies, i.d. 0.53 mm, length 5 m, thickness 0.15 μm). The temperature profile of the oven and the detector and injector temperatures were same as those used for the experiment described in Section 2.8. Equation (1) was used to calculate the yield of BDF based on the rapeseed oil weight.

2.10. Characterization

A digital camera (A570IS Powershot, Canon) connected to a microscope (Model LB, Kenis) was used to obtain microscope images of the capsules⁴⁰⁻⁵⁵. Scanning electron microscope (SEM) images of the capsule cross section were acquired⁵¹,⁵⁵. Capsule breakage was calculated after the reaction as the percentage of damaged capsules. Inductively coupled plasma atomic emission spectroscopy (ICP-7500, Shimadzu) was used to determine the concentration of calcium that leached into the FAME phase⁵⁴.

3. Results and Discussion

3.1. Properties of the Photothermal Exchange Materials

The solubility test results of the amorphous N-doped TiO₂ powders with N/Ti molar ratios from 0.05 to 0.5 with respect to the reactants indicated that none of the samples dissolved in rapeseed oil and THF, whereas the samples with N/Ti molar ratios of less than 0.2 dissolved in methanol. To address this problem, the soluble samples were hydrated further in distilled water at 313 K for 12 h to complete the hydrolysis of residual organic species and the condensation of hydroxyl groups. The treated samples were not soluble in methanol²¹. Therefore, further characterization was conducted for the N-doped TiO₂ powders with N/Ti molar ratios of 0.3, 0.4, and 0.5, and for N-doped TiO₂ pow-
Table 2 summarizes the photocatalytic activity of the N-doped TiO2 powders with different molar ratios for oxidizing acetic acid to CO2 under UV and visible light irradiation for a reaction time of 6 h. The treated samples showed a high photocatalytic activity (conversion to CO2: 14.7 %) for this reaction, whereas the samples without hydrolysis treatment had no activity. This is probably because of the removal of residual organic species from the surface and the formation of the anatase phase after hydrolysis treatment. These characterization results showed that all the changes, such as the removal of residual organic species, the formation of the anatase phase, and the improved light absorption, were related to the photocatalytic activity (Table 2). In the present study, amorphous N-doped TiO2 powder with a N/Ti molar ratio of 0.4 was selected as a suitable photothermal exchange material because this sample exhibited no photocatalytic activity and had high visible light absorption. Although the treated sample with a N/Ti molar ratio of 0.05 showed photocatalytic activity for acetic acid oxidation, this material also possesses high visible light absorption (Fig. 2) and was selected as another photothermal exchange material. The loading concentrations of the materials in the capsules were determined by the temperature rise tests.

The TiO2-supported Cr2O3 powders were also characterized by various analysis methods. XRD patterns of the prepared samples indicated that the anatase and rutile TiO2 phases derived from commercial P25 and the Cr2O3 phase were present in the samples. The amount of Cr2O3 in the prepared samples was measured by X-ray fluorescence (XRF), and the Cr loading estimated by XRF increased as the nominal Cr loading increased, and the amounts were similar to the loading calculated before preparation. The scanning electron microscope-energy dispersive X-ray fluorescence spectrometer (SEM-EDX) results also demonstrated that Cr2O3 particles were deposited uniformly on the TiO2 surface, and that the amount of Cr2O3 in the sample was estimated to be similar to the nominal loading. The UV-Vis spectra of Cr2O3/TiO2 samples showed that the transmittance in the visible and near-IR ranges decreased gradually as Cr loading increased, whereas high transparency was observed for the bare TiO2 in the visible and near-IR range from 400 to 900 nm. Thus, the addition of Cr2O3 changed the surface from white to dark green, which improved the absorption of visible and near-IR light. Because 18 wt% Cr2O3/TiO2 powder had the broadest light absorption, the photothermal exchange characteristics of this sample were investigated by evaluating the photocatalytic activity for acetic acid oxidation.

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**Table 2** Photocatalytic Activities of N-doped TiO2 Powders with Different N/Ti Molar Ratios and 18 wt% Cr2O3/TiO2 Powder for Acetic Acid Oxidation under UV and Visible Light Irradiation

| Samples  | TiO2 (P25) | TiO2-N1 | TiO2-N2 | TiO2-N3 | TiO2-N4 | TiO2-N5 | TiO2-N6 | 18 wt% Cr2O3/TiO2 |
|----------|------------|---------|---------|---------|---------|---------|---------|------------------|
|          | N/Ti = 0.05| N/Ti = 0.1| N/Ti = 0.2| N/Ti = 0.3| N/Ti = 0.4| N/Ti = 0.5|         |                  |
| Conv. to CO2 [%] | 17.2 | 14.7 | 14.7 | 2.3 | 0 | 0 | 0 | 0 |

Values are based on the results in Refs. 52) and 53).
photothermal exchange material, a CaO (100 mg/g-oil)-loaded alginate capsule, a CaO (100 mg/g-oil)-Cr₂O₃/TiO₂ powder in the capsules was 3 mg/g-oil. Because the characterization results indicated that 18 wt% Cr₂O₃/TiO₂ powder had excellent photothermal exchange characteristics, this sample was selected from the prepared TiO₂-supported Cr₂O₃ powders.

3.2. Characterization of the Capsules

Various capsules were prepared by the procedure described in Section 2.4. Figure 3 shows microscopy images of an alginate capsule without a catalyst and photothermal exchange material, a CaO (100 mg/g-oil)-loaded alginate capsule, a CaO (100 mg/g-oil)-Cr₂O₃/TiO₂ (3 mg/g-oil)-loaded alginate capsule, and a CaO (100 mg/g-oil)-active carbon (0.5 mg/g-oil)-loaded capsule. The capsule with only rapeseed oil as a core and a calcium alginate shell was transparent, indicating that light could penetrate the alginate shell and reach inside the capsule (Fig. 3(a)). In contrast, the CaO-loaded alginate capsule was white (Fig. 3(b)), which suggested that CaO powder was encapsulated. For the other capsules (Figs. 3(c) and 3(d)), the color of the core was different from that of CaO-loaded alginate capsule because of the mixture of white CaO powder and dark green Cr₂O₃/TiO₂ powder or white CaO powder and black active carbon powder. These results indicated that both powders were loaded in the capsules. The outer diameter of the prepared capsules was estimated to be around 2.0 mm from the microscope images. However, the core and the shell could not be clearly distinguished in these images. The shell thickness was estimated as 30 μm from cross-sectional SEM images (Fig. 3(e)) of CaO-loaded alginate capsules. It was confirmed that the shell thickness of the other alginate capsules was same as that (30 μm) of the CaO-loaded capsule. In contrast, the outer diameter and shell thickness of the capsules prepared by forming alginate layers consecutively followed by modification with the silane coupling agent were increased to around 4 mm and 60 μm, respectively. Thus, both the capsule size and shell thickness depended on the type of prepared capsules; however, if same preparation procedure was conducted, capsules with similar shell thickness could be obtained even though encapsulated materials were different.

Before using these capsules for the BDF synthesis reaction, the oil permeation across the capsule shell was verified. Although sesame oil, which was used instead of rapeseed oil, permeated through all the capsule shells, the amount of oil that permeated through the shell at certain times was different. This result indicated that the oil permeation rates through the capsule shells depended on the capsule types. During the static diffusion test, the concentration gradients between the inside and outside of the capsules should govern the oil permeation through the shell. Thus, the oil permeation mechanism is probably the same in all capsules because the concentration gradients of oil and 1-butanol were the same. Therefore, the different oil permeation profiles among the prepared capsules may arise from the capsule shell properties, the shell thickness, and the effect of the encapsulated material. We have previously discussed the permeation profiles in our previous papers, so we provide a brief summary here. A higher oil permeation rate was observed for the shell (thickness: 30 μm) with a single alginate layer compared with the shell (thickness: 60 μm) with several alginate layers because the shell thickness affects the oil permeation through the capsule shell. In addition, because oil permeates faster through a hydrophobic shell than a hydrophilic shell, the shell modified with silane coupling agents, which increase the hydrophobicity, had a higher oil permeation rate. Moreover, although the presence of CaO powder inside the capsule had no effect on the oil permeation rate, the co-presence of active carbon powder inside the capsule substantially reduced the permeation rates. The microscope and cross-sectional SEM images of the
shell indicated that no active carbon powder was incorporated into the capsule shell; thus, the decrease in the amount of oil that permeated through the shell was probably caused by oil adsorption on the active carbon surface via hydrophobic interactions. The FT-IR results for active carbon powder showed that there were no functional groups on this material, indicating that it was hydrophobic. Therefore, some of the encapsulated oil was probably adsorbed on the surface of the active carbon, thus slowing the permeation of the oil. We also tested the permeation of FAME across the capsule shell and found that the properties of capsule shell and type of encapsulated material affected the FAME permeation rate. Although the permeation rates depended on the capsule types, the capsules were used for BDF synthesis because the reactants and products could permeate across the shell.

3.3 Analysis of Liquid Phases Inside and Outside the Capsules

CaO-loaded alginate capsules are a promising catalyst system for the transesterification of rapeseed oil with methanol50). However, the capsule breakage by mechanical shear force reached around 20 % of the charged capsules after the first run55). To prevent mechanical breakage, the alginate shells were reinforced with silane coupling agents to form organic/inorganic hybrid capsule shells. Consecutive formation of alginate layers followed by the BTMS modification to produce dAlg-T-B capsules, which showed lower capsule breakage (2.6 %) after the first run and maintained capsule breakage of less than 20 % even after consecutive use for three runs55). The shell modification improved the rigidity of the capsules, and capsule breakage was sufficiently low. However, the induction and completion times for BDF synthesis were longer with the dAlg-T-B capsules, than with the CaO-loaded alginate capsules. The delay may be caused by the slow permeation rates of the reactants (rapeseed oil and methanol) and products (FAME and glycerin). Therefore, although relatively high capsule breakage was observed, the CaO-loaded alginate capsule was selected for further research because of its induction and completion times for BDF synthesis.

To determine the reaction mechanism of BDF synthesis with CaO-loaded alginate capsule, the liquid phases inside and outside the capsule were analyzed, and the mass transfer of reactants, intermediate species, and products were clarified55). Figure 4 shows the concentrations of reactants, intermediates, and final products during rapeseed oil methanolysis as a function of reaction time (a) in CaO-loaded alginate capsules and (b) outside CaO-loaded alginate capsules.

The capsule. During the intermediate time period (1-3 h), the methanol concentration decreased substantially, even though methanol continuously permeated into the capsule. Therefore, the permeated methanol was consumed by the methanolysis reactions immediately. Both DG and MG formed from TG methanolysis were transferred out of the capsule, whereas the majority of the FAME accumulated inside the capsule. During the end stage (3-6 h), the accumulated FAME was transferred out of the capsules and DG and MG permeated back in. DG and MG were completely converted to FAME, which gradually left the capsules. TG continuously permeated into the capsules until the TG concentration outside the capsules reached almost zero. These results indicated that the methanol permeation was important for starting and sustaining the BDF synthesis reaction with CaO-loaded alginate capsules.
Furthermore, it is likely the methanol permeation rate affected the liquid compositions inside the capsules and the reaction rates of the TG, DG, and MG methanolysis. The FAME accumulated in the capsules also functioned as a co-solvent for oil and methanol, promoting the mass transfer of these reactants into the capsules. Accordingly, a large increase in BDF yield occurred at 2-4 h for the CaO-loaded alginate capsules (Fig. 1).

The solid phase collected from the CaO-loaded alginate capsules at each reaction time was measured by XRD during the methanolysis of rapeseed oil (Fig. 5). The Ca(OH)$_2$ phase peaks were mainly observed for the solid collected at 0 h, and the Ca(OH)$_2$ phase peak intensities decreased gradually with the reaction time. However, new peaks at 2θ = 8.4° and 10.2° appeared for the solids collected at 1-6 h, and the peak intensities increased with reaction time until 4 h and then remained the same. These peaks were assigned to calcium diglyceroxide$^{17,24,26,31,50,55}$. Glycerin is a co-product of FAME during rapeseed oil methanolysis; thus, calcium diglyceroxide formation should be related to FAME production. After 1 h, the calcium diglyceroxide peaks were observed when FAME was formed in the capsules (Fig. 4). The sharp increase in the BDF yield after calcium diglyceroxide formation may indicate that this phase is the active site for BDF synthesis. The reaction scheme of the methanolysis of rapeseed oil with the CaO-loaded alginate capsules was determined from the results of the liquid and solid phase analysis (Fig. 6). The liquid and solid phase analyses showed that the main factors for sustaining BDF synthesis were the FAME accumulation in the capsules and the formation of an active phase with glycerin. The rate equations of the consecutive reaction (TG$\rightarrow$DG$\rightarrow$MG$\rightarrow$FAME) were constructed for the CaO-loaded alginate capsules and Eqs. (2)-(4) were used to calculate the pseudo first-order reaction rate constants ($K_1$, $K_2$, $K_3$). Kouzu et al. reported that when FAME is used as a co-solvent for oil and methanol, the reaction kinetics change from zero order to first order$^{22}$. The reaction kinetics of oil transesterification have also been treated as pseudo first order$^{3,61}$.

$$\frac{d[TG]}{dt} = -K_1 [TG]$$

(2)

$$\frac{d[DG]}{dt} = K_1 [TG] - K_2 [DG]$$

(3)

$$\frac{d[MG]}{dt} = K_2 [DG] - K_3 [MG] = 0$$

(4)

where $[TG]$, $[DG]$, and $[MG]$ are the concentrations of TG, DG, and MG at time $t$, respectively. The triglyceride concentration at 0-0.5 h and the concentration of the other products at 0-3 h (Fig. 4) in the capsules were used. The rate constants $K_1$, $K_2$, and $K_3$ were evaluated as $1.4 \times 10^{-3}$ [s$^{-1}$], $1.7 \times 10^{-3}$ [s$^{-1}$], and $1.4 \times 10^{-2}$ [s$^{-1}$], respectively. Therefore, TG methanolysis was the rate-determining step in rapeseed oil transesterification with methanol using the CaO-loaded alginate capsules.

In Fig. 1, the CaO-loaded alginate capsule system showed a faster reaction rate than the CaO powder catalyst. Therefore, the reason why this capsule system had a higher activity than the CaO catalyst was discussed. In the conventional CaO powder catalyst, the induction period usually occurs when the amount of FAME generated in a batch reactor is sufficiently high to mix oil and methanol homogeneously$^{22}$. The accumulation of FAME inside the capsules would be much more rapid than for the CaO powder catalyst because the total capsule volume is much smaller than that of
the reactor. Therefore, the CaO-loaded alginate capsules had a shorter induction period. Another possible reason is the ease of forming the calcium diglyceroxide phase as an active site for BDF synthesis\(^{71,24,26,31,50,55}\). Because glycerin dissolves partially in FAME and methanol but not in oil\(^{62}\), the glycerin took some time to move out of the capsules. Therefore, greater contact frequency between the CaO catalyst and glycerin was possible inside the capsules compared with the CaO powder catalyst in a batch reactor because the total capsule volume was much smaller. As a result, the formation of the calcium diglyceroxide phase was accelerated inside the capsule, which increases the reaction rate. These two reasons explain why the CaO-loaded alginate capsules showed a higher reaction rate than the CaO powder catalyst.

### 3.4. Performance of Various Capsules for BDF Synthesis under Condensed Light Irradiation

In previous work, we performed the methanolysis of rapeseed oil to FAME with CaO (100 mg/g-oil)-active carbon (2.0 mg/g-oil)-loaded alginate capsule under light irradiation without a condenser lens\(^{51}\). This capsule system exhibited a BDF yield of about 80 % after 6 h at a temperature of 308 K. The light-driven methanolysis of rapeseed oil was achieved because the active carbon powder absorbed visible and near-IR light, and transferred the heat in the capsules, which resulted in a higher temperature inside the capsules than in the reaction mixture. In addition, the amount of Ca species leached into the FAME phase was reduced substantially compared with the CaO powder catalyst or the CaO-loaded alginate capsule because of the lower reaction temperature\(^{51}\). Although the capsules containing the catalyst and photothermal exchange material are promising in terms of BDF yield and Ca leaching, it was suggested that the irradiation power affected the final BDF yield. The active carbon was characterized to clarify this point; however, the results were not sufficient to draw a conclusion. Therefore, we prepared and characterized a photothermal exchange material that absorbs a wide range of irradiated light, similar to active carbon powder, and capsules containing this material were used for BDF synthesis under condensed light irradiation with different types of light (power from 0.6 to 3.6 W). The photothermal exchange materials absorb different ranges of irradiated light, for example amorphous N-doped TiO\(_2\) powder absorbs UV and part of the visible range, whereas active carbon and Cr\(_2\)O\(_3\)/TiO\(_2\) powders absorb a wide range from UV to near-IR. First, we confirmed that using two types of N-doped TiO\(_2\) powders with photocatalytic activity affected the photothermal exchange and BDF yield. As mentioned earlier, both amorphous N-doped TiO\(_2\) powder with a N/Ti molar ratio of 0.4 and N-doped TiO\(_2\) powder (treated) with a N/Ti molar ratio of 0.05 were selected as photothermal exchange materials. The treated powder has a high photocatalytic activity, whereas the untreated powder has no photocatalytic activity under UV and visible light irradiation. In a preliminary test\(^{52}\), when the methanolysis of rapeseed oil was conducted with the prepared capsules under condensed light irradiation with a full wavelength range (3.6 W), the BDF yield was in the order CaO-amorphous N-doped TiO\(_2\) (N/Ti = 0.4, 3 mg/g-oil)-loaded capsules; CaO-18 wt% Cr\(_2\)O\(_3\)/TiO\(_2\) (3 mg/g-oil)-loaded capsules; CaO-amorphous N-doped TiO\(_2\) (N/Ti = 0.05)-loaded capsule. Thus, the untreated powder with no photocatalytic activity behaved as a photothermal exchange material, increasing the temperature in the capsules, which led to a higher BDF yield than using the CaO-loaded capsule. In contrast, the treated powder with photocatalytic activity decomposed the organic compounds in the capsules or produced byproducts, which decreased the BDF yield. Based on these results, we concluded that amorphous N-doped TiO\(_2\) powder that has no photocatalytic activity should be used as a photothermal exchange material for BDF synthesis. However, after 6 h the final BDF yield of 40 % was lower than the final BDF yield (80 %) with CaO-active carbon-loaded capsules (Fig. 7). This is probably because amorphous N-doped TiO\(_2\) powder absorbs a much narrower range of wavelengths than the active carbon powder. To address this problem, TiO\(_2\)-supported Cr\(_2\)O\(_3\) powders with various Cr loadings were prepared, and 18 wt% Cr\(_2\)O\(_3\)/TiO\(_2\) powder was selected as a suitable photothermal exchange material. Moreover, because this material could be characterized sufficiently, the effect of irradiation power on the final BDF yield would be clear. Therefore, CaO-Cr\(_2\)O\(_3\)/
TiO₂-loaded capsules were used for rapeseed oil methanolysis with irradiation powers of 3.6, 2.1, 1.1, and 0.6 W corresponding to the full wavelength range, IR range, IR range with a slit, and the IR range with a slit and mesh, respectively. The capsule breakage after 6 h was around 30 % in all cases based on the initial amount of the capsules. Moreover, the reaction mixture collected after the removal of capsules showed no activity for BDF synthesis, suggesting that the reaction occurred in the capsules. The BDF yield for the CaO-Cr₂O₃/TiO₂-loaded capsules was higher than that obtained with the CaO-loaded capsules under the full wavelength range of light irradiation (Fig. 7). It was confirmed in the preliminary tests that Cr₂O₃/TiO₂-loaded and alginate capsules exhibited no activity for BDF synthesis under the same reaction conditions. These results indicate that CaO powder was the active catalyst for BDF synthesis and that Cr₂O₃/TiO₂ acted as a photothermal exchange material that maintained a higher temperature in the capsules than in the reaction media (defined as outside the capsules). Moreover, the final BDF yield after 6 h decreased from 70 to 40 % when the light irradiation power was decreased from 3.6 to 0.6 W. In addition, similar BDF yields were obtained with the same light irradiation power (0.6 W) regardless of the light range. Therefore, the final BDF yield depended on the irradiation power because Cr₂O₃/TiO₂ powder has the same absorption properties from 200 to 900 nm. However, it was unclear how the irradiation power affected the BDF yield. The temperature of the reactants in the CaO-18 wt% Cr₂O₃/TiO₂-loaded capsules under condensed light irradiation with irradiation power from 0.6 to 3.6 W was measured indirectly by a thermograph. The results indicated that the temperature after 5 min of irradiation strongly depended on the irradiation power, and the temperatures were 299.8, 305.2, 328, and 350 K (Fig. 8(c)) for powers of 0.6, 1.1, 2.1, and 3.6 W, respectively. In all cases, the temperature at 0 min was 293 K. Because the experimental conditions for temperature observation were different from that for BDF synthesis, it was not possible to compare the observed temperatures with the temperatures achieved during BDF synthesis directly. However, the trend in the temperature reached after 5 min of irradiation was related to the BDF yield, which changed from 40 to 70 %, with an increase in the irradiation power from 0.6 to 3.6 W. It was concluded from the results that the most important factor for increasing the BDF yield in the CaO-Cr₂O₃/TiO₂-loaded capsule system was the temperature in the capsules, which was affected by the irradiation power.

For the CaO-active carbon-loaded capsules, first the effect of a condenser lens on the BDF yield was tested with the CaO (100 mg/g-oil)-active carbon (2.0 mg/g-oil)-loaded capsules with and without a condenser lens. Surprisingly, although the temperature of the reaction media reached 315 K (higher than the set temperature), a lower final BDF yield of 46.9 % was obtained with a condenser lens. In contrast, a final BDF yield of 80 % was obtained without a condenser lens. The temperature in the capsules under light irradiation without a condenser lens has been reported as 323 K after 300 s of irradiation, but with a condenser lens it reached 363 K after 82 s (Fig. 8(e)). These results suggest that although a higher temperature inside the capsules was achieved with a condenser lens, a lower BDF yield was obtained. This unexpected result could be explained by the higher capsule breakage (73 %, Table 3) caused by a rapid increase in the temperature inside the capsules, which results in the loss of the reaction field for the rapeseed oil methanolysis. After the capsules break, the reaction proceeds in the reaction media; therefore, the reaction media temperature affected the final BDF yield for this capsule system. For this reason, although the light irradiation with a condenser lens provided a sufficiently high temperature in the capsules for BDF synthesis, higher capsule breakage reduced the BDF yield. Therefore, the temperature in the capsules during BDF synthesis should be controlled by varying the concentrations of the encapsulated active carbon and the irradiation power. To optimize the active carbon loading, the capsules loaded with various
concentrations (0.1-2.0 mg/g-oil) of the active carbon powder were tested for the BDF synthesis under condensed light irradiation (3.6 W). The results indicated that the BDF yield at 1 h was increased from 18.3 to 59.8 % by decreasing the active carbon loading from 2.0 to 0.5 mg/g-oil\(^5\). In addition, the final BDF yield was also increased from 46.9 to 90 % by decreasing the active carbon loading from 2.0 to 0.5 mg/g-oil\(^5\). Although the temperatures in the capsules with active carbon loadings of 0.5 mg/g-oil and 1.0 mg/g-oil were not obtained by the thermograph, the order of the internal temperatures are likely to be 2.0\(^1\) > 1.0\(^2\) > 0.5 mg/g-oil loading because the estimated capsule breakages after 6 h were 73, 68, and 53 % for loadings of 2.0, 1.0, and 0.5 mg/g-oil, respectively (Table 3). Based on the internal capsule temperature and the capsule breakage, the CaO-active carbon (1.0 mg/g-oil)-loaded capsule was expected to have a higher BDF yield than CaO-active carbon (0.5 mg/g-oil)-loaded capsules; however, these results were not obtained. Another parameter, the permeation of reactants through the capsule shell, was considered to explain this observation. Lower oil permeation was achieved for capsules with a higher active carbon loading. Thus, the permeability of the reactants through the capsule shell is also an important parameter to explain the different performance between CaO-active carbon (1.0 mg/g-oil)-loaded capsules and CaO-active carbon (0.5 mg/g-oil)-loaded capsules.

In contrast, CaO-active carbon (0.1 mg/g-oil)-loaded capsules showed a fairly high BDF yield of 60 % at 1 h and 76 % at 6 h\(^5\). We described the reaction steps for rapeseed oil methanolysis with CaO-loaded alginate capsules in Section 3.3. In a preliminary test\(^5\), analysis of the liquid phases inside and outside the capsules suggested that similar reaction steps occurred with CaO-active carbon (0.5 mg/g-oil)-loaded capsules under condensed light irradiation (Fig. 9). Therefore, we discuss the performance further based on these reaction steps. A lower capsule breakage (49 %) and higher oil permeation were achieved with the CaO-active carbon (0.1 mg/g-oil)-loaded capsules, whereas the temperature inside the capsules may be lower than that of CaO-active carbon (0.5 mg/g-oil)-loaded capsules. The internal capsule temperature reached 343 K after 300 s of irradiation and remained constant for 20 min. Moreover, the capsule breakage during the BDF synthesis remained similar, at 44 % for 1 h and 49 % after 6 h. These results indicated that most capsule breakage happened early in the reaction, and that the temperature inside the capsules was constant during the rest of the reaction. To explain this behavior, the heat capacities of the reactants (rapeseed oil: 1800 J mol\(^{-1}\) K\(^{-1}\); methanol: 83.3 J mol\(^{-1}\) K\(^{-1}\); and THF: 124.2 J mol\(^{-1}\) K\(^{-1}\)) and the product (methyl oleate: 666.4 J mol\(^{-1}\) K\(^{-1}\)) should be considered. Although pure rapeseed oil was encapsulated in the original capsules, methanol and THF entered the capsules, and rapeseed oil left. Thus, the heat capacity of the core solution decreased considerably compared with the original composition, resulting in the rapid increase of the temperature inside the capsules during the initial period up to 1 h. Consequently, the BDF synthesis reaction proceeded with the CaO catalyst, while the capsule breakage happened. In contrast, once the production of DG, MG, and FAME began, the core composition was a mixture of rapeseed oil, methanol, THF, and FAME. The temperature in the capsules stabilized gradually because the core composition of the capsules reached a steady state. Thus, during the intermediate and end periods, the capsule breakage was suppressed and the temperature was constant. In both the CaO-active carbon (0.5 mg/g-oil)-loaded capsule and CaO-active carbon (0.1 mg/g-oil)
Thus, a higher final BDF yield at 1 h and 6 h because the reaction field was maintained. The temperature inside the capsules was the most important factor for the BDF yield at 1 h. However, the temperature inside the capsules was the most important factor for the BDF yield at 1 h. Consequently, the CaO-loaded capsule exhibited a higher reaction rate than the CaO powder catalyst.

For the CaO-photothermal exchange material-loaded capsules, first a material that absorbed a wide range of irradiated light was selected. The effect of the irradiation power on the BDF yield was compared for CaO-loaded capsules, TiO$_2$ powder and active carbon powder as photothermal exchange materials. An increase in the irradiation power increased the temperature in the capsules, resulting in a higher BDF yield. Considering the BDF yield, capsule breakage, the temperature inside the capsule, the permeation rates of the reactants and products, and the amount of Ca leached into the FAME phase, the CaO-active carbon (0.5 mg/g-oil)-loaded capsule was the best capsule system. This system had the highest BDF yield (90 %) among the prepared capsules under condensed light irradiation with a full wavelength range (3.6 W).

Figure 7 shows the best performance of various CaO-photothermal exchange material-loaded capsules for the BDF synthesis under condensed light irradiation with a full wavelength range, and Fig. 8 shows the temperatures in the different capsules, which were measured indirectly with a thermograph, under light irradiation. In addition, the capsule breakage of those capsules after 6 h is summarized in Table 3.

Finally, the amount of Ca that leached into the FAME phase for CaO-active carbon (0.5 mg/g-oil)-loaded capsules under condensed light irradiation with a full wavelength range after 6 h was calculated based on the ICP results. ICP analysis results showed that the concentration of Ca dissolved into the FAME phase was 18.7 ppm, which was corresponding to the amount of 0.25 mg. The amount of CaO catalyst charged in the capsules was 0.096 g, it was estimated that the FAME phase contained 0.37 % Ca from the CaO catalyst, which was comparable to the values (0.3-0.7 %) obtained with CaO-loaded capsules for BDF synthesis using a mantle heater. In addition, this amount of Ca (0.37 %) was similar to that (0.48 %) in the FAME phase obtained with CaO-active carbon (2 mg/g-oil)-loaded capsules under light irradiation without a condenser lens. From these results, we concluded that CaO-active carbon (0.5 mg/g-oil)-loaded capsule is the most promising catalyst system for the BDF synthesis under condensed light irradiation with a full wavelength range.

4. Concluding Remarks

The methanolysis of rapeseed oil with various capsules was conducted. Analyzing the liquid and solid phases inside and outside the CaO-loaded capsules showed that the accumulation of FAME and the formation of CaO-glycerin complex phase were important factors in sustaining the BDF synthesis reaction. Because the total capsule volume was much smaller than that of the reactor, the accumulation of FAME inside the capsule was much faster than for the CaO powder catalyst, and the formation of the active complex phase was accelerated inside the capsule as well. Consequently, the CaO-loaded capsule exhibited a higher reaction rate than the CaO powder catalyst.

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要 旨

CaO 内包アルギン酸カプセルを用いたバイオディーゼル燃料の合成

古澤 毅

宇都宮大学大学院工学研究科、321-8585 栃木県宇都宮市陽東7-1-2

CaO 内包アルギン酸カプセルを用いて菜種油のエステル交換反応による BDF 合成を検討した。カプセル内外の液相分析およびカプセル内部の固相分析を行った結果、共溶媒として作用する FAME のカプセル内部での蓄積、および副生グリセリ
ンと CaO による複合体の形成が BDF 合成反応において重要な因子であることが分かった。また、CaO 砂糖とともに、光熱変換物質をカプセル内部に内包すると、従来のマントルヒーターによる加熱方法を用いず、光エネルギー照射下で十分に BDF 合成反応が進行することも分かった。さらに、カプセル内部温度は照射する光の量に依存し、光量の増加に伴ってカプセル内部温度が上昇することを確認した。種々の検討結果より、
CaO（100 mg/g-oil）と活性炭（0.5 mg/g-oil）を内包したカプセルを、全光照条件（全波長領域、集光レンズあり、3.6 W）下での BDF 合成反応へ適用すると、1 時間で 60 %、6 時間で 90 %
の BDF 収率を達成し、最も良い性能であった。また、同条件下でのカプセル破損率は 53 % であったものの、FAME 相への Ca 溶出率はわずか 0.37 % であった。