**A novel solid base catalyst for transesterification of triglycerides toward biodiesel production:
carbon nanohorn dispersed with calcium ferrite**

Noriaki Sano^{*}, Kohei Yamada, Shoichi Tsunauchi, Hajime Tamon

Department of Chemical Engineering, Graduate School of Engineering,

Kyoto University, Katsura, Nishikyo-ku, Kyoto, 615-8510, Japan

Abstract: Carbon nanohorn (CNH) dispersed with a calcium ferrite $\text{Ca}_2\text{Fe}_2\text{O}_5$ ($\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH}$) was synthesized as a new catalyst, and its superior catalytic activity to convert a triglyceride to a fatty acid methyl ester via transesterification reaction was demonstrated. The process to prepare this catalyst has three steps as follows. For the first step, Fe-dispersed CNH (Fe-CNH) was synthesized by a gas-injected arc-in-water method. For the second step, the oxidation treatment in diluted CO_2 or in air was performed on Fe-CNH to transform Fe nanoparticles dispersed in Fe-CNH to Fe_3O_4 or Fe_2O_3 , respectively. For third step, Fe_3O_4 -dispersed CNH ($\text{Fe}_3\text{O}_4\text{-CNH}$) or Fe_2O_3 -dispersed CNH ($\text{Fe}_2\text{O}_3\text{-CNH}$) was co-calcined with $\text{Ca}(\text{NO}_3)_2$, resulting to the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH}$. The powdery catalysts of $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH}$ can be recovered by magnetic field for recycled use. In the transesterification experiment, tricaprylin was converted to methyl caprylate. The reaction rate of this transesterification

^{*} Corresponding author. Tel: +81 75 383 2684; fax: +81 75 383 2654. *E-mail address:* sano@cheme.kyoto-u.ac.jp (N. Sano)

using $\text{Ca}_2\text{Fe}_2\text{O}_5$ -CNH catalysts was obviously higher than using conventional CaO catalyst. Also CNH supporting CaO without including Fe (CaO-CNH) was prepared, and this catalyst exhibited a high catalytic activity for this transesterification. However, CaO-CNH did not have the property for magnetic recovery. Among the catalysts prepared here, $\text{Ca}_2\text{Fe}_2\text{O}_5$ -CNH prepared using Fe_3O_4 -CNH as precursor exhibited the highest reaction rate for the transesterification. The hybridization of the calcium ferrite possessing basic sites with hydrophobic CNH was considered to be the key factor for its high catalytic performance.

Key words: carbon nanohorn, biodiesel, catalyst, transesterification, calcium ferrite

1. Introduction

Biodiesel produced from triglycerides and fatty acids contained in waste oils or non-edible plant oils receives intensive attention to decrease consumption of fossil resources. Transesterification of triglyceride and esterification of free fatty acid (FFA) with methanol can generate fatty acid methyl ester (FAME), and FAME is considered to be useful for biodiesel fuel [1-3]. It is important to choose

appropriate catalysts to realize transesterification and esterification for the efficient biodiesel production. It is widely known that a variety of heterogeneous base and acid catalysts can be useful to catalyze the transesterification and esterification, respectively [4-7]. Conventionally, homogeneous liquid catalysts, e.g. NaOH or H₂SO₄, have been used to produce biodiesel [8, 9]. However, in the use of such conventional liquid catalysts, there is a serious drawback in difficult recovery of catalysts from reaction solutions, corrosive character, and soap formation [10], resulting in strong motivation to develop high-performance heterogeneous solid catalysts.

In many cases, solid catalysts consist of small reactive crystal particles and catalyst support materials to stabilize such highly-dispersed crystal particles, by which the surface area of the reactive crystals can be enlarged [11-14]. Among the catalyst support materials, carbon can be effective due to its chemical stability and controllable structures [13,14]. Recently, carbon nanotube-family materials are investigated to use for catalyst support for this purpose [14-16]. Among them, carbon nanohorn (CNH) [17] would be a promising material to prepare the biodiesel-production catalysts, and it was reported that sulfonated CNH and Fe-dispersed CNH (Fe-CNH) showed a high performance to catalyze the biodiesel production by the esterification of FFA [14, 18]. However, these acid catalysts have low catalytic activities for transesterification of triglycerides [14], which are main components in many kinds of feed stocks.

In this study, using Fe-CNH as a precursor, new solid base catalysts consisting of a calcium ferrite supported by CNH was synthesized to catalyze transesterification of triglycerides for biodiesel

production. The catalytic performance of this catalyst was evaluated by a transesterification experiment to produce methyl caprylate from tricaprylin. Here, this catalytic activity was compared with that of CaO-supported CNH and a conventional CaO catalyst. In addition, key factors in the catalyst preparation method are discussed based on some structural characterizations on the carbon-based precursors.

2. Experimental

2.1 Catalyst preparation

Fe-CNH, used as a precursor, was synthesized by a gas-injected arc-in-water (GI-AIW) method [19-21]. This method can prepare CNH dispersed with metallic nanoparticles either unalloyed or alloyed in one step when metallic components are included in graphite anode. In this method, arc discharge is generated in a holey graphite cathode submerged in water with N₂ injection into arc plasma zone, and the anode is vaporized by a hot arc plasma so that the nano-size structures are constructed by rapid quenching of vaporized anode components. The condition to synthesize Fe-CNH in this study including the electrode dimensions are as follows: A graphite rod (diameter = 6 mm) on which a hole (diameter = 1.5 mm; depth = 60 mm) was drilled along its axis to host Fe wire (diameter = 1.45 mm; length = 60 mm) was used as an anode. A graphite rod (diameter = 20 mm; length = 50 mm) with a co-axial hole (diameter = 12 mm; length = 25 mm) at its bottom and four channels (diameter = 2 mm) on its top to introduce N₂ gas was used as a cathode. The speed to insert the anode into the cathode

bottom hole was constant at 1.8 mm/s to sustain the arc discharge (100 A, 30 V).

Recently, it is reported that a heat treatment in diluted CO₂ (CO₂/N₂ = 1/9 in volume) can be conducted on Fe-CNH to make its carbonaceous part porous and to oxidize Fe in Fe-CNH to ferrimagnetic Fe₃O₄ [22]. To prepare the catalyst in the present study, Fe-CNH synthesized by GI-AIW method was subject to this treatment. In this treatment, Fe-CNH was placed in a cylindrical furnace in the abovementioned diluted CO₂ environment. The temperature there was raised to 1000°C with an elevation rate of 10°C/min, and this temperature was sustained for 1 h. By this treatment, Fe nanoparticles dispersed in Fe-CNHs turned to be ferrimagnetic Fe₃O₄ almost completely. Therefore, Fe-CNHs oxidized by this treatment can be referred to as Fe₃O₄-CNHs.

It is known from previous reports that the porosity of CNH can be highly improved by heat treatment in air [22-24]. This treatment was also applied to Fe-CNH here. Fe-CNH was placed in the cylindrical furnace in ambient air, and the temperature there was raised to 380°C with a temperature elevation rate of 10°C/min. Then this temperature was sustained for 30 min. By this treatment, Fe nanoparticles dispersed in Fe-CNH became paramagnetic Fe₂O₃. Thus, Fe-CNH after this treatment is referred to as Fe₂O₃-CNH.

Fe₃O₄-CNH and Fe₂O₃-CNH was co-calcined with Ca(NO₃)₂ to prepare the catalysts consisting of CNH supporting a calcium ferrites, which was identified to be Ca₂Fe₂O₅ as explained later. These catalysts are referred to as Ca₂Fe₂O₅-CNH. In this step, approximately 0.5 g of Fe₃O₄-CNH or Fe₂O₃-CNH was admixed to a Ca(NO₃)₂ aqueous solution with stirring for 4 h in room temperature. There,

the concentration of $\text{Ca}(\text{NO}_3)_2$ in the solution was adjusted so that CaO/CNH weight ratio became 0.6. Subsequently, this mixture was dried at 120°C . After drying, the mixture was calcined in Ar at 850°C for 4 h. By this calcination, $\text{Ca}(\text{NO}_3)_2$ seemed to react with Fe_3O_4 in $\text{Fe}_3\text{O}_4\text{-CNH}$ and Fe_2O_3 in $\text{Fe}_2\text{O}_3\text{-CNH}$, resulting in the transformation of Fe_3O_4 and Fe_2O_3 to the ferrite of $\text{Ca}_2\text{Fe}_2\text{O}_5$.

For comparison, the same process of the co-calcination with $\text{Ca}(\text{NO}_3)_2$ was applied on the as-grown Fe-CNH without any oxidation treatment. In addition, CNH synthesized by GI-AIW method without inclusion of Fe also was subject to this co-calcination process. Then, as explained later, CaO crystal particles were supported on Fe-CNH and CNH, respectively. The catalyst prepared here can be referred to as CaO/Fe-CNH and CaO-CNH, respectively. The abbreviations of the catalyst support CNH, the CNH-based precursors, and the catalysts prepared in this study are tabulated in Table 1 with brief explanations of the synthesis methods. The catalysts prepared using $\text{Fe}_3\text{O}_4\text{-CNH}$ and $\text{Fe}_2\text{O}_3\text{-CNH}$ are named to be $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ and $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//air}$, respectively.

Furthermore, conventional catalyst, CaO crystal fine powder, was prepared by thorough milling. A commercial CaO crystal powders of analytical grade (Waco Chemical) were crushed by a rigid-rotor crusher (Osaka Chemical, Newpower mill PM2005) driven by 1380 W power, when the resulted particle size of CaO became $0.5\text{-}1.0\ \mu\text{m}$. A calcination in Ar was performed on these milled CaO powders in 850°C for 4 h to make dehydration and decarboxylation.

2.2 Characterizations of the catalyst properties

The structures of the CNH-based precursors and catalysts prepared in this study were analyzed

by a transmission electron microscope (TEM) (JEOL, JEM1010). Their surface areas and pore structures were evaluated by N₂ adsorption at -196°C by an automatic analyzer (Bel Japan, Belsorp-mini). Their crystal structures were analyzed by a X-ray diffractometer (XRD) (Rigaku, RINT2100). The magnetic properties of the catalysts synthesized here and the precursors were evaluated by measurement of AC magnetic susceptibility using a magnetometer (Magqu Co., XacQuan-II) at room temperature.

A CO₂ temperature programmed desorption (TPD) analysis was performed on four catalysts synthesized in this study, Ca₂Fe₂O₅-CNH//CO₂, Ca₂Fe₂O₅-CNH//air, Ca-CNH, and CaO, using an automatic TPD analyzer (MicrotracBEL, BELCAT). In this analysis, CO₂ diluted with He (CO₂ concentration = 4.86 %) was used for analysis gas. The specimen was dried in He at 400°C for 30min, subsequently the specimen was cooled to 50°C for saturated adsorption of CO₂. The temperature elevation rate was set to be 10 °C/min to reach 900°C for desorption of CO₂.

2.3 Transesterification experiment using tricaprylin

In this study, tricaprylin was used as a model compound for transesterification with methanol to obtain methyl caprylate, considering that generally the transesterification of triglycerides with methanol is a part of biodiesel production. A three-neck flask mounted with a Dimroth condenser was used as a batch reactor. Tricaprylin (3.0 g), methanol (3.0 g), one of the catalysts prepared were put

into this reactor, and they were mixed by a magnetic stirring bar (500 rpm). The weight of a catalyst $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ put into this reaction solution was 0.12 g, and the weights of the other catalysts were adjusted so that the weight of Ca in the solution can be the same as the case of $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$. This reactor was warmed in a temperature-controlled bath at 64°C, and the reaction was continued up to 5 h duration.

The components in the solution in the reactor were monitored by a gas chromatograph (Shimadzu, GC14B) equipped with a flame ionization detector using an adsorbent column (GL Science, Support: Uniport C, Liquid phase: Unisole 3000, mesh range: 80/100). In this chromatography analysis, the temperature at the adsorbent column was changed from 100°C to 340°C with elevation rate of 10°C/min after the sample of 0.1 μm was injected. The yield of the trasesterificaiton of tricaprilin to produce methyl caprylate, $Y [\%]$, is defined by the percentage of the mole of methyl caprylate produced by the experiment among the mole of the methyl caprylate which can be theoretically produced with complete conversion of the feed.

3. Results and discussion

3.1 Structures of ferrite-CNH catalysts and key properties of precursors

Some examples of the TEM images of the CNH-based precursors and catalysts prepared in this study are shown in Fig. 1. This figure shows the structures of (a) as-grown CNH without Fe-inclusion, (b) Fe-CNH, (c) $\text{Fe}_3\text{O}_4\text{-CNH}$, (d) $\text{Fe}_2\text{O}_3\text{-CNH}$, (e) $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//air}$, and (f) Ca-CNH. A TEM image

of $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ is shown in Fig. 2.

It can be seen in Fig. 1a that CNH is consisting of carbonaceous closed horns highly aggregated one another, forming a nearly spherical particles of diameter 50-100nm. These particles again tend to make secondary aggregation. In Fig. 1b, one can see that Fe particles of about 20 nm diameter and other Fe particles of much smaller than that are dispersed in Fe-CNH. The weight percentage of Fe in Fe-CNH was measured by weighing the residue of specimen after removing carbonaceous part by complete burning in thermal gravimetry analysis (TG) (Shimadzu, TGA-50). As confirmed by an X-ray diffractometer (XRD), Fe was completely oxidized to Fe_2O_3 , so the weight percentage of Fe in Fe-CNH was calculated by taking stoichiometric relation of Fe to Fe_2O_3 into account. As a result, the weight of Fe in Fe-CNH were estimated to be 15.9%.

Though the carbonaceous part in Fe-CNH can obtain small pores by the oxidation step in diluted CO_2 environment as investigated later, the main structure of CNH in the Fe-CNH is not destroyed by this oxidation treatment, as seen in Fig. 1c. In this oxidation treatment, the weight of carbonaceous part was partially lost, and the burn-off weight percentage of the carbonaceous part was 19 %.

In the case of oxidation treatment in air, a part of Fe-CNH was destroyed, and aggregated Fe_2O_3 particles can be seen in Fig. 1d. In this oxidation treatment, the weight loss of carbonaceous part was larger than that in the oxidation in diluted CO_2 environment, and the burn-off weight percentage of the carbonaceous part reached 32 %.

After the step of co-calcination of $\text{Fe}_3\text{O}_4\text{-CNH}$ with $\text{Ca}(\text{NO}_3)_2$, nearly spherical particles with

diameter of about 50 nm appeared, as shown in Fig. 2. These particles were identified to be a calcium ferrite $\text{Ca}_2\text{Fe}_2\text{O}_5$, as explained later. Fig. 2 shows a result analyzed by an energy-dispersive X-ray (EDX) equipped at a scanning transmission electron microscope (STEM) (JEOL, JEM2100F) on $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$. It is shown that a larger particle pointed by P contains Ca, Fe and O with the same shape of distribution, suggesting that such particles are alloy oxide particles with uniform component distribution. Small particle pointed by Q seemed to be consisting of only Fe. However, the portion of such unalloyed Fe particles should be fairly low because the XRD analysis did not detect them as mentioned later.

When $\text{Fe}_2\text{O}_3\text{-CNH}$ was co-calcined with $\text{Ca}(\text{NO}_3)_2$, the particles of 50 nm appeared similarly to the case of $\text{Fe}_3\text{O}_4\text{-CNH}$. Such particles should be $\text{Ca}_2\text{Fe}_5\text{O}_5$ as well as when $\text{Fe}_3\text{O}_4\text{-CNH}$ was co-calcined. Nevertheless, it should be reminded that carbonaceous part of Fe-CNH was partially destroyed by the oxidation treatment in air, and Fe_2O_3 particles were aggregated then. Thus, the aggregates of $\text{Ca}_2\text{Fe}_5\text{O}_5$ which were not supported by CNH should coexist in the specimen of $\text{Ca}_2\text{Fe}_2\text{O}_5\text{//air}$.

In addition, the TEM images of CaO/Fe-CNH and CaO-CNH were similar to those of $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ in the point that the particles of about 50 nm diameter were seen. Fig. 1f shows an example of TEM images of Ca-CNH . It should be noted that such particles are not ferrite but CaO .

The BET surface area per unit mass of carbonaceous part in the specimen obtained by the N_2 adsorption is summarized in Table 1. It is shown that the specific surface area of Fe-CNH can be significantly increased by the both oxidation treatments in $\text{CO}_2\text{-N}_2$ environment and in air. This

increase of the specific surface area is considered to be caused by opening pores at weak points on horn structures of CNH (i.e. five carbon ring at tip of horn). This pore opening can make the void inside carbonaceous horn available for N₂ adsorption so that the mesopore volume can be significantly increased by this structural change [23,24].

Table 1 shows the mesopore volume of each specimen evaluated by a method proposed by Dollimore and Heal [25], where one can see the increase of the mesopore volume caused by the oxidation treatments. Because the most of metallic nanoparticles synthesized by GI-AIW method are migrated in carbonaceous part of CNH [22], the pores opened by these oxidation treatments should promote the oxidative gases to diffuse in CNH so that Fe nanoparticles therein can be oxidized. In this study, it should be emphasized that these pores may also play a role as channels for transportation of key components to produce the calcium ferrite. This hypothesis can be supported by the results by XRD analysis as explained later that the step of the co-calcination with Ca(NO₃)₂ can lead to the formation of the calcium ferrite only when the Fe-CNH was treated by the oxidation treatment, and Fe particles in Fe-CNH can be kept unalloyed unless Fe-CNH was subject to the oxidation treatments.

It can be seen that the BET surface area and mesopore volume became significantly smaller after the co-calcination with Ca(NO₃)₂ was carried out in all cases. This result suggests that calcium ferrites or CaO may partially cover the pores on the catalyst supports.

XRD patterns of the catalyst support (CNH), precursors (Fe-CNH, Fe₃O₄-CNH, Fe₂O₃-CNH), and the catalysts prepared in this study (Ca₂Fe₂O₅-CNH//CO₂, Ca₂Fe₂O₅-CNH//air, CaO/Fe-CNH,

CaO-CNH, CaO) are summarized in Fig. 3. Here, pristine powders of Fe, Fe₂O₃, and Fe₃O₄ are also shown as references. It can be confirmed that oxidation treatment in diluted CO₂ environment on Fe-CNH leads to the oxidation of Fe in Fe-CNH to ferrimagnetic Fe₃O₄ without generating paramagnetic Fe₂O₃. There, no pristine Fe remains. In contrast, the oxidation treatment in air leads to the oxidation of Fe to paramagnetic Fe₂O₃, exclusively. The origin of the selectivity for generating Fe₃O₄ or Fe₂O₃ depending on the gas environment is explained elsewhere from thermodynamic viewpoint [22]. To bring about the oxidation to either Fe₃O₄ or Fe₂O₃, the gas components CO₂ or O₂ must be able to diffuse to Fe nanoparticles inside carbonaceous part of Fe-CNHs. The pore-opening by the oxidation treatments, which is mentioned above, should help this diffusion.

The XRD patterns of CaO-CNH and CaO/Fe-CNH commonly show the peak of CaO at 32.5°, 37.5°, and 54°, suggesting that CaO can be supported on CNH and Fe-CNH by co-calcination with Ca(NO₃)₂. As seen in the XRD pattern of CaO/Fe-CNH, unalloyed Fe can remain there after the co-calcination step. Also, it should be recognized that no calcium ferrite is detected in Ca/Fe-CNH. These results would be because most of the Fe nanoparticles in Fe-CNH are protected by carbon so that Fe can hardly react with Ca(NO₃)₂. It should be noted that two prominent peaks appeared in XRD pattern around 44° and 51° after the co-calcination step. From the appearance of these new peaks, it can be considered that the co-calcination step may induce to generate Ca-C compounds. Wu et al. suggested that calcium carbide-driven carbons (CCDCs) can exhibit the XRD peak around 44° [26].

It should be emphasized that the peak corresponding Fe₃O₄ and CaO were not detected in both

$\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ and $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//air}$. Instead, new peaks appear at 33.5° and 46.6° . These new peaks correspond a calcium ferrite, $\text{Ca}_2\text{Fe}_2\text{O}_5$ [27]. This result suggests that almost all the Fe_3O_4 and Fe_2O_3 dispersed in $\text{Fe}_3\text{O}_4\text{-CNH}$ and $\text{Fe}_2\text{O}_3\text{-CNH}$ were converted to this ferrite. In these cases, Fe_3O_4 and Fe_2O_3 should react with $\text{Ca}(\text{NO}_3)_2$ in the co-calcination step via the pores opened by the aforementioned oxidation treatment on $\text{Fe}_3\text{O}_4\text{-CNH}$ and $\text{Fe}_2\text{O}_3\text{-CNH}$.

One can see many peaks in the XRD patterns of $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ and $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//air}$ except the peaks indicating $\text{Ca}_2\text{Fe}_2\text{O}_5$. Because the peak around 35.5° , which is the major peak suggesting Fe_2O_3 or Fe_3O_4 , is not seen, these peaks should not indicate the existence of Fe_2O_3 or Fe_3O_4 although these peaks partially match the XRD patterns of Fe_2O_3 or Fe_3O_4 . Also, the peak around 37.5° , which is the major peak suggesting CaO , is hardly seen, CaO should not be included there. It is regret that the structure indicated by these peaks have not yet been identified by searching literatures to our best effort. Nevertheless, a peak shown around 44° may suggest the production of CCDCs in $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ and $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//air}$.

3.2 Magnetic properties of catalysts

AC magnetic susceptibilities of Ca-CNH , Ca/Fe-CNH , $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ and $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//air}$ are shown in Fig. 4. From view point of the magnetic recovery of the catalysts for repeated use, the values of real number of the AC susceptibility at very low frequency should be carefully observed. From this result, one can expect that the catalysts prepared here can be attracted by magnets except Ca-CNH . Fig. 5 shows that $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH}$ can be captured by magnets. The high magnetic

susceptibility is preferable to recover these powdery catalyst quickly. Thus, Ca/Fe-CNH and $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ should have the suitable property for the magnetic recovery.

3.3 Transesterification experiment to convert triacylglycerin to methyl caprylate

Fig. 6 shows the comparison of the performance of the catalysts prepared in this study for biodiesel synthesis by showing the change of the yield of methyl caprylate from triacylglycerin as a function of reaction time. It can be seen that $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ exhibits the highest reaction rate and the yield can achieve 100%. In the present condition, the yield by this catalyst reaches about 95% in 120 min, and can become close to 100% within 180 min. The next superior catalyst is CaO-CNH, by which reaction rate seems about 88 % in 120 min and can become close to 100% in 240 min. $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//air}$ achieves 66% in 120 min, and this yield is significantly lower than the yield by $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ and CaO-CNH. Nevertheless, the yield by this catalyst can reach close to 100% in 300 min.

In contrast to these yields, it seems that there is a limit in the yield obtained using conventional CaO catalyst, where the yields does not seem to reach above 80% even if the reaction duration is further extended. The origin of this limitation of the yield can be considered from deactivation of the catalysts. It is reported that CaO can react with glycerol, which is generated from the transesterification of triglycerides as a by-product, and then CaO is transformed to calcium glycerolate [28], resulting in the deactivation of the conventional CaO catalyst.

One may wonder why the CaO-CNH can exhibit a high catalytic activity, although the

catalytic activity of conventional CaO is fairly limited. For this reason, it should be recognized that the surface of CaO is very hydrophilic, so that the glycerol, which is also hydrophilic, can preferably be adsorbed on the surface of CaO to produce calcium glyceroxide there. Note that the formation of glyceroxide at the CaO surface cause deactivation of its catalytic activity. In case of CaO supported on CNH, CaO particles can be surrounded by hydrophobic CNH when CaO-CNH are agglomerated. In such structures, glycerol produced at the CaO surface by the catalytic transesterification would be expelled out from the narrow zones in the CaO-CNH aggregates. Therefore, the deactivation of the catalytic activity of CaO-CNH can be retarded, resulting to the high yield of nearly 100%. Also in the early time when deactivation is still low, the reaction rate of transesterification with CaO-CNH can be promoted by expelling the hydrophilic byproduct of glycerol out from the catalytic site because of the surrounding hydrophobic CNH, so that the reaction rate is so high.

The effect of removing glycerol byproduct from catalytic site due to hybridization with hydrophobic CNH should occur also in the cases using $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ and $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//air}$. In the case of $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$, the catalytic activity becomes the highest as mentioned above because of this effect. However, reaction rate of the transesterification with $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//air}$ is relatively low even though this catalyst consists of hydrophilic $\text{Ca}_2\text{Fe}_2\text{O}_5$ hybridized with hydrophobic porous CNH. To consider this reason, the porous structures should be compared, which can be seen in Table 1. The BET surface area and mesopore volume of $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//air}$ is almost twice as those of $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$. This result suggests that opening pores does not always help to increase the

catalytic activity, but opening pores excessively leads to the decrease of the effect of removing hydrophilic byproduct from catalytic site because of lack of hydrophobic carbonaceous surfaces.

The catalytic activity of the transesterification using CaO/Fe-CNH is the lowest among the catalysts prepared in this study, where the reaction rate is the lowest and the yield is limited to below 75%. The XRD pattern of CaO/Fe-CNH may suggest a hint for this reason. As mentioned above, two new prominent peaks appeared in the XRD pattern when CaO/Fe-CNH was prepared from Fe-CNH by the co-calcination with $\text{Ca}(\text{NO}_3)_2$. This result can suggest that significant portion of $\text{Ca}(\text{NO}_3)_2$ is converted to undesired products, one of which is CCDs, resulting that only limited portion of $\text{Ca}(\text{NO}_3)_2$ is transformed to CaO.

Recently, there is an article reporting that CaFe_2O_4 - $\text{Ca}_2\text{Fe}_2\text{O}_5$ -based catalyst consisting of mixture of two types of calcium ferrites can be potential catalyst for biodiesel catalyst [29]. In our case, it is unique that the newly-developed catalyst can exhibit the superior catalytic activity for transesterification for biodiesel production, and the reason of such high reactivity can be ascribed to the hybridization of the calcium ferrite possessing the basic sites with the hydrophobic CNH.

Reusability of the catalyst developed here was investigated as shown in Fig. 7. In this experiment, the catalyst ($\text{Ca}_2\text{Fe}_2\text{O}_5$ -CNH// CO_2) was recovered using a magnet for repeated use. Under this condition, the yield of 100% was kept for three times, and it decreased to 86.6% at fifth time. The decrease of the yield should be partially ascribed to the loss of catalyst particles when they are recovered, and may be due to deactivation. Detail analysis of the reusability of this catalyst will be

conducted in future to improve the stable usage.

3.4 CO₂ temperature programmed desorption (TPD) analysis on catalysts

The TPD charts of this analysis are shown in Fig. 8, and the temperature of the TPD peak and basic site concentration are tabulated in Table 2. It is found that Ca₂Fe₂O₅-CNH//CO₂, which showed the highest catalytic activity, does not have the highest TPD peak temperature. In addition, the basic site concentration of Ca₂Fe₂O₅-CNH//CO₂ is the lowest among the catalysts shown here. These results can support the hypothesis that the strength of the basic site of Ca₂Fe₂O₅-CNH may not be the determinant factor for its high catalytic performance. Instead, it could be considered that the hybridization of hydrophilic ferrite possessing basic sites with the hydrophobic CNH in the catalyst structure can be the key property to exhibit the high catalytic performance.

4. Conclusions

A new catalyst to promote transesterification of triglycerides to obtain FAME, which is CNH dispersed with a calcium ferrite Ca₂Fe₂O₅, has been synthesized. This catalyst has ferrimagnetic property so that this catalyst can be recovered by magnetic field. This catalyst was synthesized using Fe-CNH synthesized by GI-AIW method as a precursor, and Fe-CNH was treated by oxidation in diluted CO₂ or in air to transform Fe nanoparticles in Fe-CNH to Fe₃O₄ or Fe₂O₃, respectively. By co-calcination with Ca(NO₃)₂, the both Fe₃O₄-CNH and Fe₂O₃-CNH were transformed to Ca₂Fe₂O₅-CNH. Among them, Ca₂Fe₂O₅-CNH//CO₂ has higher magnetic susceptibility and catalytic activity than CaFe₂O₄-CNH//air. Both of the catalysts can exhibit higher catalytic performance than conventional

CaO catalyst, and especially $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ can exhibit higher catalytic activity than CaO-CNH.

Note that CaO-CNH without inclusion of ferrite cannot be recovered by magnet.

The structural characterization of the catalysts ($\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$, $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//air}$, CaO/Fe-CNH, CaO-CNH and CaO) and CNH-based precursors (Fe-CNH, $\text{Fe}_3\text{O}_4\text{-CNH}$ and $\text{Fe}_2\text{O}_3\text{-CNH}$) were carried out. It was speculated that the pores opened by oxidation treatment on carbonaceous part of $\text{Fe}_3\text{O}_4\text{-CNH}$ and $\text{Fe}_2\text{O}_3\text{-CNH}$ would be important for the formation of the ferrite in the catalysts. It was considered that the hybridization of the ferrite possessing the basic sites with the hydrophobic CNH in the catalyst structure should be the key property to exhibit the high catalytic performance. This hybridization may realize the effect by which hydrophilic glycerol byproduct formed at the catalytic site can be removed because of the aggregating hydrophobic CNH, so that the catalytic site can be kept active in the process of the transesterification reaction.

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Table 1 Specific surface area and mesopore volume of catalyst support, CNH-based precursors and the catalysts prepared in this study.

specimen	synthesis method	BET surface area [m ³ /g-CNH]	mesopore volume [cm ³ /g-CNH]
CNH	GI-AIW method using graphite anode	263.2	1.68
Fe-CNH	GI-AIW method using graphite anode containing Fe wires	301.4	2.76
Fe ₃ O ₄ -CNH	oxidation on Fe-CNH in diluted CO ₂ (CO ₂ /N ₂ = 1/9, 1000°C)	659.1	12.29
Fe ₂ O ₃ -CNH	oxidation on Fe-CNH in air (400°C)	942.8	14.41
CaO-CNH	co-calcination of CNH with Ca(NO ₃) ₂	176.3	0.51
CaO/Fe-CNH	co-calcination of Fe-CNH with Ca(NO ₃) ₂	196.8	0.62
Ca ₂ Fe ₂ O ₅ -CNH//CO ₂	co-calcination of Fe ₃ O ₄ -CNH with Ca(NO ₃) ₂	274.4	1.68
Ca ₂ Fe ₂ O ₅ -CNH//air	co-calcination of Fe ₂ O ₃ -CNH with Ca(NO ₃) ₂	534.2	3.06

Table 2 Results from TPD analysis on four catalysts prepared in this study.

Catalyst	Temperature at TPD peak [°C]	Basic site concentration [mmol/g-catalyst]
CaO	777	3.61
CaO-CNH	791	5.15
Ca ₂ Fe ₂ O ₅ -CNH//CO ₂	761	2.35
Ca ₂ Fe ₂ O ₅ -CNH//air	756	4.21

Fig. 1. TEM images of (a) CNH synthesized by GI-AIW method, (b) Fe-CN synthesized by GI-AIW method, (c) Fe_3O_4 -CNH synthesized from Fe-CN by oxidation treatment in diluted CO_2 , (d) Fe_2O_3 -CNH synthesized from Fe-CN by oxidation treatment in air, (e) high magnification image of $\text{Ca}_2\text{Fe}_2\text{O}_5$ -CNH//air, and (f) CaO-CN.

Fig. 2. Result of line analysis of STEM and TEM image of $\text{Ca}_2\text{Fe}_2\text{O}_5$ -CNH// CO_2 . The line A-B correspond the position analyzed by STEM.

Fig. 3. Summary of the XRD patterns of the catalyst support (CNH), CNH-based precursors (Fe-CNH, Fe_3O_4 -CNH, Fe_2O_3 -CNH), catalysts prepared in this study ($\text{Ca}_2\text{Fe}_2\text{O}_5$ -CNH// CO_2 , $\text{Ca}_2\text{Fe}_2\text{O}_5$ -CNH//air, Ca/Fe-CNH, Ca-CNH, CaO), and pristine metals for reference (Fe, Fe_3O_4 , Fe_2O_3).

Fig. 4. AC magnetic susceptibility of four catalysts prepared in this study. χ_{Re} and χ_{Im} are real number and imaginary number of complex number of AC magnetic susceptibility of the catalysts.

Fig. 5. Photograph of $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ attracted by magnets in ethanol

Fig. 6. Yield of transesterification of tricaprylin to obtain methyl caprylate, Y , related with reaction time using the catalysts prepared in this study.

Fig. 7. Yield of transesterification of tricaprylin to obtain methyl caprylate, Y , in reusability test using $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ as a catalyst with a reaction condition of weight of tricaprylin = 3g, weight of methanol = 3g, and weight of $\text{Ca}_2\text{Fe}_2\text{O}_5\text{-CNH//CO}_2$ = 0.12 g.

Fig. 8. CO₂ TPD charts of four catalysts prepared in this study.

Graphical Abstract