Calcium-Loaded Municipal Sludge-Biochar as an Efficient and Stable Catalyst for Biodiesel Production from Vegetable Oil

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ABSTRACT: In this contribution, biochar from municipal sludge was used as a novel matrix for the synthesis of a series of calcium-based heterogeneous catalysts toward biodiesel production. Their catalytic activity was investigated in terms of catalyst loading and calcination temperature during preparation, in addition to the transesterification parameters including the methanol/oil molar ratio, reaction time, and catalyst amount. The highest biodiesel yield up to 93.77% was achieved with the 30Ca/A-SBC-700, and it maintained as high as 84.9% even after 10 cycles of a consecutively alternating catalysis and regeneration process. It was revealed that the porous municipal sludge biochar and autologous SiO2 were accountable for the superior stability of the present catalyst. This work may provide a new path to value-added valorization of sludge waste and also a renewable and efficient catalyst for biodiesel production at a low cost.

1. INTRODUCTION

Currently, the depletion of fossil energy and the historically high atmospheric level of greenhouse gas have raised the urgent needs for renewable energy. Among many alternative fuels, biodiesel is regarded as a competent choice due to its ecofriendly nature and sustainable concerns. Generally, industrial synthesis of biodiesel follows the homogeneous transesterification of vegetable oils (animal fats, algal oil, etc.) and C1−C2 alcohols catalyzed by KOH, NaOH, and H2SO4. However, the strong acidity and basicity of these catalysts can be quite corrosive to reactors. Furthermore, it is quite difficult to recycle these homogenous catalysts from the reaction products after synthesis, not to mention the complex purifying process prior to second use, thus both leading to an increased economic cost. In this context, there are growing interests in the development of a heterogeneous catalyst because of their easy separation and weak corrosion.

In contrast to the longer time and higher temperature required for acid-catalyzed transesterification processes, basic catalysts are apparently more appealing for the same end. In particular, calcium oxide (CaO) has gained wide interests by virtue of its strong basicity, low cost, wide availability, mild reaction conditions, and less impact on the environment compared with its sodium- and potassium-based counterparts. CaO from abalone shells, eggshells, and other wastes have been reported as an economical strategy for construction of biodiesel catalysts. Of note, the loss of CaO due to ion leaching and deactivation caused by chemical transformation into Ca(OH)2 and CaCO3 are potential factors that may impair the overall efficiency. To address it, various binary metal oxide-formed calcium composites (Mg/Ca, Ca/Ce, Ca/Al, etc.) are developed aiming to promote the stability of CaO catalysts where the intensive interactions between different metal oxides would prevent Ca2+ from leaching into the mobile phase during biodiesel production. Yet, these alien metal ions may also suffer from similar leaching problems. Besides, the nonferrous metals would finally, to some extent, lead to an enhanced capital cost of biodiesel catalysts. Therefore, several recent works have diverted to the stabilization of Ca catalysts with nonmetal agents. For instance, silicon/silicon oxides are reported as effective additives. An optimized bimodal meso-macroporous silica-supported calcium oxide, referred to as 50CaO/B-325, was revealed with a maximum FAME yield up to 94.5% and retained 88.87% after five repeated catalytic processes. Also, Chen et al. reported hybrid oxides of calcium and silicon oxides from eggshells and Na2SiO3. The %FAME was revealed as 90.2% and remained as 81% after 10 catalysis cycles. By using natural diatomite as matrix for the CaO catalyst, Shan et al. reported that the formation of the Ca−O−Si bond may account for the enhanced stability of the Ca/Si hybrid catalyst.

Municipal sludge is the main waste generated from sewage treatment process. It is generally accepted that pyrolysis is the
most rapid and effective way to reduce its volume and environmental impact; yet, to achieve full utilization remains a great challenge in practical due to very limited out path for the solid byproduct, namely, the biochar.\textsuperscript{22} Biochars are well-known to possess wide variety of surface functional groups and hierarchical porosity, which provide tremendous available sites for surface modification.\textsuperscript{23–26} Several researches have demonstrated the potential of woody and bone biochars as support for the transesterification catalyst.\textsuperscript{27–30} The catalytic performance, including activity and stability, is largely related to their components, surface properties, and porosities, among others, which are well summarized in previous reviews.\textsuperscript{31–33} Despite the existence of a considerable amount of SiO\textsubscript{2} in municipal sludge in China, rare attention have been paid to the potential of this feature in fabricating a catalyst for the biodiesel synthesis. Herein, this work, to our best knowledge, for the first time exploited waste municipal sludge biochar as novel matrix for construction of a series of CaO-based heterogeneous catalysts. The physiochemical properties of attained catalysts were characterized with SEM, TGA, EDS, FTIR, \textit{N}\textsubscript{2} isothermal adsorption/desorption, etc. Also, detailed investigation was then carried out in terms of calcium loading, calcination temperature, methanol/oil molar ratio, reaction time, and so on.

2. EXPERIMENTAL SECTION

2.1. Materials and Reagents. Municipal sludge was provided by the local wastewater treatment plant. KOH, CaO, tetrahydrofuran, methanol (analytical grade) were purchased from Aladdin reagent (Shanghai) co. LTD. Palm oil was from a local market in Guangzhou City (Guangdong Province, China).

2.2. Preparation and Activation of the Sludge Biochar (SBC). The fresh municipal sludge was desiccated at 105 °C before being pulverized with a ball mill. Then, the collected solids was sifted with a mesh. Such sludge powder was transferred into a tube furnace and calcined under 800 °C for 30 min at a ramping rate of 10 °C/min under an inert atmosphere. After naturally cooling down to room temperature, the SBC was collected. In a typical activation operation, 2 g of S-BC was added into 500 mL 2 mol/L KOH solution and drastically agitated for 1 h. The suspension was then subjected to repeated filtration with deionized water. Finally, the activated sludge biochar (A-SBC) layer was oven-dried at 105 °C overnight.

2.3. Preparation of the Biochar-Based Catalyst. To obtain the catalyst for biodiesel synthesis, the above A-SBC was then fully mixed with different 20, 30, and 40 wt % CaO suspensions. Typically, in the case of 20 wt % CaO suspension, 2 g CaO was dispersed in 100 mL deionized water followed by the addition of dried A-SBC. The aqueous mixture was rapidly stirred prior to desiccation for 24 h. After that, the dry solid was calcined under 600, 700, and 800 °C for 2 h. The thus-attained catalyst was denoted as \textit{mCa}/A-SBC-\textit{T}, where \textit{m} wt % and \textit{T} referred to the mass fraction of CaO suspension and calcination temperature.

2.4. Biodiesel Synthesis. Palm oil (30 g), together with suitable amount of catalyst and methanol were added into a 150 mL three-necked, round-bottomed flask. Then, the mixture was kept at 65 °C and magnetically stirred for a set period. After then, the catalyst was easily removed by centrifugation, and the supernatant was kept still for hours. The resultant waste was absorbed by sodium sulfate and excessive methanol, while the former was removed by centrifugation and the latter could be removed by evaporation. Finally, the obtained biodiesel (fatty acids methyl ester, FAME) was analyzed with gas chromatography (GC), and the corresponding yield was calculated as follows:

\[
\text{biodiesel yield} = \frac{\text{weight of biodiesel} \times \% \text{FAME}}{\text{weight of oil}} \times 100\%
\]

where %FAME is the concentration of FAME attained from GC analysis.\textsuperscript{34}

2.5. Catalyst Stability Test. To test the reusability of the as-prepared catalyst, the used catalyst collected by centrifugation was fully rinsed by tetrahydrofuran and dried at 105 °C. Then, the regenerated catalyst was again used for biodiesel synthesis under the same reaction conditions. This operation was repeated 10 times.

2.6. Characterizations. Thermogravimetric analysis (TG) was carried out with a SDT Q600 thermogravimetric analyzer. Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) were conducted with QUANTA 200 at the accelerating voltage of 20 kV. XRD patterns are acquired with X-ray diffractometry (XRD-Bruker; D8 Advance) coupled with Cu K\textalpha\ radiation. Textural properties were obtained and analyzed with \textit{N}\textsubscript{2} isothermal adsorption and desorption on an Autosorb1-MP Quantachrome. Fourier transform infrared spectroscopy was performed with a Bruker equipment, Alpha model.

3. RESULTS AND DISCUSSION

3.1. Synthesis Procedure. Figure 1 gives the synthesis procedures of calcium-loaded biochar catalysts (\textit{mCa}/A-SBC-

\[
\text{Pyrolysis KOH Activation}
\]

\[
\text{Municipal Sludge} \quad \text{SBC} \quad \text{A-SBC}
\]

\[
\text{Mixing with} \quad \text{m wt % CaO dispersion} \quad \text{Before} \quad \text{calcination} \quad \text{m=20, 30, 40%}
\]

\[
\text{mCa}/A-SBC-T \quad \text{mCa}/A-SBC
\]

Figure 1. Synthesis procedure from municipal sludge to the calcium-loaded biochar catalysts, \textit{mCa}/A-SBC-T, \textit{m} = 20, 30 and 40%, \textit{T} = 600, 700 and 800 °C.

\text{T} from municipal sludge. The desiccated fresh municipal sludge appeared as dark brown solids, which then totally turned into black during pyrolysis and KOH activation. After mixing with \textit{m} wt % CaO dispersions (\textit{m} = 20, 30, or 40%), a slightly increased contrast were identified with \textit{mCa}/A-SBC-\textit{T} and \textit{mCa}/A-SBC-T, in which the \textit{T} refers to the calcination temperature, namely, 600, 700, and 800 °C. Then, a series of calcium-loaded biochar catalysts were obtained for biodiesel production from palm oil.

3.2. Morphology and Textural Properties. Figure 2 provides the SEM images of (a) SBC, (b) A-SBC, and (c) 30Ca/A-SBC-700 catalysts. The initial SBC revealed a rough yet solid surface. Upon activation by KOH, the yielding A-SBC demonstrated an obvious porous surface, which can be attributable to both the collapse of carboxylic structures assisted by K\textsuperscript{+} and consumption of those instable carbon structures via reactions with OH. After calcium loading, the 30Ca/A-SBC-700 maintained similar roughness with A-SBC,
whereas a substantial decrease of surface voids was noticed, accompanied with the emergence of cauliflower-like particulates. To have more information on elemental transition, the EDS analysis was applied simultaneously, and the results are summarized in Table 1. Three points were randomly selected in each sample. The SBC was mainly composed of C, O, Si, and Al, and the carbon content slightly decreased after activation (seen from the results of A-SBC), which is reasonable according to the above analysis. With further impregnation with CaO suspensions and calcination, a noticeable increased Ca content was found, manifesting the successful calcium loading.

**Table 1. EDS Analysis of the SBC, A-SBC, and 30Ca/A-SBC-700 Catalyst**

| picture text point | C  | O  | Si | K  | Ca | Mg | Al | others |
|--------------------|----|----|----|----|----|----|----|--------|
| Figure 1a A       | 37.97 | 47.76 | 7.12 | 0.54 | 0.93 | 0.57 | 5.10 | 0.01   |
| B                 | 36.42 | 50.82 | 6.68 | 0.48 | 0.94 | 0.49 | 4.16 | 0.01   |
| C                 | 34.87 | 50.40 | 6.94 | 0.60 | 0.68 | 0.51 | 6.01 | 0.01   |
| Figure 1b A       | 35.83 | 53.11 | 5.48 | 0.51 | 0.48 | 0.36 | 4.23 | 0      |
| B                 | 35.40 | 43.92 | 9.91 | 2.18 | 0.83 | 0.37 | 7.39 | 0      |
| C                 | 32.89 | 52.31 | 7.53 | 0.72 | 0.72 | 0.56 | 5.28 | 0.01   |
| Figure 1c A       | 16.95 | 56.09 | 10.28 | 1.03 | 7.63 | 0.62 | 7.40 | 0      |
| B                 | 32.10 | 55.94 | 4.19 | 0.17 | 3.33 | 0.38 | 3.90 | 0.01   |
| C                 | 26.60 | 53.36 | 12.17 | 0.46 | 2.52 | 0.48 | 4.41 | 0      |

Figure 3 presents the XRD patterns of A-SBC, 30Ca/A-SBC-600, 30Ca/A-SBC-700, 30Ca/A-SBC-800, 20Ca/A-SBC-700, and 40Ca/A-SBC-700. The diffraction peaks at 22, 26.6, 50, and 59° were assigned to the featured signals of SiO$_2$ according to the standard JCPDS files. Meanwhile, the newly appeared signals peaking at 32.5, 37.6, and 54° in calcium-impregnated mCa/ASD-T indicated that CaO were successfully loaded onto the A-SBC matrix. Moreover, the signals of CaO gradually intensified as the calcination temperature increased from 600 to 800 °C. This can be ascribed to the thermal decomposition of Ca(OH)$_2$ at high temperature. Besides, a small peak at 42.6° is indicative of the formation of Ca$_2$SiO$_4$ from CaO and autologous SiO$_2$ of A-SBC. However, the patterns of other Ca-loaded catalysts revealed no signals of Ca$_2$SiO$_4$. This could be explained from two facts: First, SiO$_2$ content in this SBC is nearly half of that in peat biochar, which provides less amount of available SiO$_2$ for Ca$_2$SiO$_4$. Second, since the SiO$_2$ are dispersed in the carbon matrix, therefore the loss of carbon species at a higher calcination temperature may allow the exposure of more SiO$_2$ and lead to formation of more Ca$_2$SiO$_4$, accordingly with a notable diffraction peak.

FTIR spectra of SBC, A-SBC, and 30Ca/A-SBC-700 catalysts recorded with a wavenumber ranging from 500 to 4000 cm$^{-1}$ are given in Figure 4. The former two displayed quite similar characteristic adsorption behaviors, suggesting the negligible influence on chemical groups of SBC by the slight activation process. The obviously wide adsorption bands at 3436 cm$^{-1}$ are attributable to the stretching vibration of hydroxyls, while the adsorptions locating at 1637 cm$^{-1}$ is likely to arise from the vibration of C=O structures. Besides, the notable adsorptions around 1054 cm$^{-1}$ were assigned to the vibrations of Si–O–Si bonds. The new adsorption at 1454 cm$^{-1}$ in 30Ca/A-SBC-700’s profile can be assigned to the vibrations of carbonate ions, which may form from the slight chemical adsorption of CO$_2$. Furthermore, a new peak at 991 cm$^{-1}$ suggested the formation of Ca$_2$SiO$_4$.

The TG and TGA profiles of A-SBC and 30Ca/A-SBC-700 catalysts recorded in a nitrogen atmosphere are shown in Figure 2.
Figure 4. FTIR spectra of SBC, A-SBC, and 30Ca/A-SBC-700 catalysts.

Figure 5. It should be stated that the mass loss below 100 °C is owing to the evaporation of H2O, which may be absorbed by the samples during preparation and transfer. A-SBC revealed negligible overall weight loss across the temperature range from 100 to 700 °C, suggesting the excellent thermal stability. On the contrary, the profile of 30Ca/A-SBC-700 displayed two obvious drops at 390 and 550 °C, respectively. Meanwhile, the first sharp drop with weight loss by 5% at a lower temperature can be assigned to the dehydration reaction of Ca(OH)2 upon heating. As the temperature keeps increasing, CaCO3 started to decompose into CaO and CO2, which was expressed as a wide slope in the recorded curve. Generally, both products showed good thermal stability as the overall weight loss was below 9%. Besides, the textural properties of all samples were investigated with the isothermal nitrogen adsorption and desorption, and the results are listed in Table 2. The activation treatment by KOH led to a slightly enlarged specific surface area; however, further calcium loading caused a sharp decrease. It is reasonable that introducing CaO onto the surface may fill or cover voids, thus result in the loss of available interface.

3.3. Optimization of the Catalytic Activity of A-SBC-Based Catalysts. In order to reveal the influence of catalyst preparation on their final catalytic properties, a series of calcium-loaded catalysts were prepared with designed parameters (CaO weight fraction of 0–40 wt % and calcination temperature at 600–800 °C). To be specific, the parameters for the transesterification process are as follows: SBC and A-SBC shared parameters, including a reaction time of 300 min, catalyst amount of 10 wt %, and methanol/oil molar ratio at 12:1, while that for 20Ca/A-SBC-700 were 240 min, 7 wt %, and 9:1, respectively. Parameters for 30Ca/A-SBC-700 were 150 min, 5 wt %, and 8:1. Parameters for 40Ca/A-SBC-700 were 150 min, 5 wt %, and 8:1. Parameters for 30Ca/A-SBC-600 were 180 min, 6 wt %, and 9:1. Parameters for 30Ca/A-SBC-800 were 180 min, 6 wt %, and 8:1. Consequently, the corresponding biodiesel yield for each catalyst is listed in Figure 6. As seen from the columns, the yield significantly increased from 14.49 to 93.77% with CaO loading increasing from 0 to 30 wt %. Since basic components in biochars instead of acid are reasonable for their catalytic activity.41 Therefore, the observed limited catalytic activity of pristine SBC should have stemmed from those K and Ca species. On the other hand, the significantly enhanced basicity with CaO loading was accountable for greatly promoting the catalytic activity. Yet, with a further increased CaO loading to 40 wt %, the corresponding yield slightly dropped to 92.43%; this can be explained by the agglomeration effect by the excess amount of CaO, which led to a decreased specific surface area and importantly a negligible increase or even blocked active sites. The calcination temperature is also revealed to be of vital importance. As it increased from 600 to 800 °C, the biodiesel yield first rose from 91.49 to 93.77% and then decrease to 89.21%. In association with the textural properties, this result is likely to originate from the nearly halved specific surface area, which significantly reduced the available interface required for multiphase reactions over heterogeneous catalysts. Accordingly, it is clear that the optimal parameters for such biochar-

Table 2. Textural Properties of SBC, A-SBC, and Calcium-Loaded A-SBC

| catalyst          | SBC   | A-SBC  | 20Ca/A-SBC-700 | 30Ca/A-SBC-600 | 30Ca/A-SBC-700 | 30Ca/A-SBC-800 | 40Ca/A-SBC-700 |
|------------------|-------|--------|----------------|----------------|----------------|----------------|----------------|
| specific surface area (m²/g) | 147.240 | 159.371 | 89.764         | 86.948         | 83.048         | 50.645         | 71.536         |
| pore volume (cc/g)    | 0.2410 | 0.2563 | 0.1844         | 0.193          | 0.1825         | 0.1100         | 0.1774         |
| average pore size (nm) | 32.7405 | 32.1619 | 41.0834        | 44.3876        | 43.9530        | 43.4283        | 49.59          |

Figure 6. Biodiesel yield of SBC, A-SBC, 30Ca/A-SBC-600, 30Ca/A-SBC-700, 30Ca/A-SBC-800, 20Ca/A-SBC-700, and 40Ca/A-SBC-700.
supported CaO catalysts were 30 wt % CaO loading in addition to the calcination temperature of 700 °C.

3.4. Influence of Transesterification Parameters on Biodiesel Yield. Three transesterification parameters including the methanol/oil molar ratio, reaction time, and catalyst amount are investigated to see their effect on the biodiesel yield. For comparison, 30Ca/A-SBC-600, 30Ca/A-SBC-700, and 40Ca/A-SBC-700 catalysts were used in the transesterification process.

The reaction time and catalyst amount for 30Ca/A-SBC-600, 30Ca/A-SBC-700, and 40Ca/A-SBC-700 were sequentially set as 180 min and 6 wt %, 150 min and 5 wt %, and 150 min and 5 wt %. The biodiesel yield versus the methanol/oil molar ratio is then plotted in Figure 7. As the methanol/oil molar ratio increased, the yield went up simultaneously and came to a maximum value around 8–9%. Then, it slightly dropped with a higher ratio. This is reasonable since an excess amount of methanol added into the reaction flask would dilute the overall concentration of other reagents and also the catalyst, which thereby deliver a reverse effect.8

In another set of experiments, the reaction time was tuned from 30 to 240 min, while the methanol/oil molar ratio and catalyst amount for 30Ca/A-SBC-600, 30Ca/A-SBC-700, and 40Ca/A-SBC-700 were sequentially set as 9:1 and 6 wt %, 8:1 and 5 wt %, and 8:1 and 5 wt %. The biodiesel yield as a function of reaction time is presented in Figure 8. At the reaction time of 30 min, the lowest conversion rate near 50% was achieved among three catalysts. Then, all the yield gradually went up as reaction continues. The maximum yield for 30Ca/A-SBC-600, 30Ca/A-SBC-700, and 40Ca/A-SBC-700 were 91.49, 93.77, and 92.43%, whereas the reaction time required were 180, 150, and 180 min, respectively. Further prolonged reaction witnessed a slight decreased yield. Considering that transesterification is a typical reversible chemical process, the yield may slightly fluctuate due to the reverse transesterification after an equilibrium was achieved.

The catalyst amount is not only an important parameter for transesterification reaction itself, but also a vital factor for practical use as it may directly influence overall cost-effectiveness. In this case, the catalyst amount was thereby set as the variable, which varied from 3 to 10 wt %, while the methanol/oil molar ratio and reaction time for 30Ca/A-SBC-600, 30Ca/A-SBC-700, and 40Ca/A-SBC-700 were 9:1 and 180 min, 8:1 and 150 min, and 8:1 and 150 min, respectively. As shown in Figure 9, the biodiesel yield rapidly went up as more catalysts were added. The optimal amount for 30Ca/A-SBC-600, 30Ca/A-SBC-700, and 40Ca/A-SBC-700 were 6, 5, and 6 wt %, respectively. Additionally, the biodiesel yields went down with overuse of the catalysts. As for the reaction system, the addition of solid catalysts may lead to enhanced viscosity, which therefore deteriorates the mass transfer process.42

3.5. Catalyst Stability. Catalyst stability determines the service period. Herein, it is assessed by monitoring the variation of the biodiesel yield as a function of the time of reuse. In addition of afore-used 30Ca/A-SBC-600, 30Ca/A-SBC-700, and 40Ca/A-SBC-700, a pure CaO catalyst was also included for comparison. Also, all catalysts were reused for additional nine cycles following the same regeneration process. The reaction parameters, including the reaction time, methanol/oil molar ratio, and catalyst amount for the above four catalysts are given as follows: 30Ca/A-SBC-600 (180 min, 9:1, and 6 wt %), 30Ca/A-SBC-700 (150 min, 8:1, and 5 wt %), 40Ca/A-SBC-700 (150 min, 8:1, and 5 wt %), and pure CaO catalyst (180 min, 9:1, and 5 wt %). As shown in Figure 10, the biodiesel yields for all four catalysts declined with repeated use. Especially, the value for the pure CaO catalyst exhibited the largest drop by nearly 30% after 10 catalysis cycles, while the drop for 30Ca/A-SBC-600, 30Ca/A-SBC-700, and 40Ca/A-SBC-700 were around 15.13, 8.86, and 12.66%, respectively. These facts are due to the loss of Ca2+ active materials during the transesterification reactions.37,43
Nevertheless, it clearly verified the positive effect of biochar matrix, which enabled the superior stability of the heterogeneous CaO catalyst, and demonstrated the best stability of 30Ca/A-SBC-700 in addition to the highest catalyst activity.

In addition, the XRD patterns of fresh 30Ca/A-SBC-700 and recovered 30Ca/A-SBC-700 after 10 catalysis cycles were provided in Figure 11. The characteristic diffractions of SiO$_2$, CaO, and Ca$_2$SiO$_4$ were easily identified in both two patterns. Furthermore, since there is no detectable peak shifts observed with the catalyst before and after reuse, the crystalline structures of every inorganic oxides and salts should have been well reserved during the transesterification process. Meanwhile, the intensity of all peaks showed negligible variations, which is indicative of a very limited loss of the crystalline materials. Thus, the excellent stability was attributable to both the stabilization by biochar matrix and the minerization of CaO with SiO$_2$, where the former played a major role. On the whole, the heterogeneous catalyst was well maintained throughout the whole reaction and regeneration process, which is particularly beneficial to industrial production.

3.6. Comparison with Reported Catalysts. The catalytic performance of 30Ca/A-SBC-700 and previously reported calcium/SiO$_2$ composite catalysts and their corresponding reaction parameters are listed in Table 3. Compared with the artificial zeolite, natural diatomite or other biochar-supported counterparts, the present municipal sludge biochar is competent in either the biodiesel yield or reaction conditions. In addition to the negative environmental effects of the raw material, this novel catalyst could be particularly meaningful to achieve the value-added valorization of sludge.

4. CONCLUSIONS

To sum up, a novel calcium-loaded municipal sludge biochar composite was facilely synthesized and demonstrated as an excellent heterogeneous catalyst for biodiesel production from vegetable oil. The optimal catalyst 30Ca/A-SBC-700 in terms of catalytic properties and stability was obtained with 30 wt % CaO loading prior to calcination at 700 °C, and it outperformed those previously reported CaO/SiO$_2$ composite catalysts in the biodiesel yield, reaction time, molar ratio, and catalyst amount. Moreover, after 10 cycles of alternate use and regeneration, the crystalline structures of 30Ca/A-SBC-700 are well preserved, which accordingly enabled the biodiesel yield of 84.9%. The biochar matrix and protogenetic SiO$_2$ have contributed to the good stability. On the whole, this work had demonstrated an innovation for municipal sludge valorization and a renewable, efficient catalyst for transesterification at a low cost.

Table 3. Comparison of the 30Ca/A-SBC-700 Catalyst with Other Reported Solid Base (SiO$_2$) Derived Catalysts

| catalyst support | temperature (°C) | molar ratio | time (min) | catalyst loading (wt %) | biodiesel yield (%) | reference |
|------------------|-----------------|-------------|------------|-------------------------|---------------------|-----------|
| Ca/SBA-15        | 200             | 6:1         | 480        | 5                       | 99.1                | 44        |
| CaO/SiO$_2$      | 65              | 9:1         | 180        | 5                       | 90.2                | 20        |
| CaO/SiO$_2$      | 65              | 9:1         | 240        | 7                       | 91.5                | 45        |
| CaO/SiO$_2$      | 65              | 9:1         | 150        | 6                       | 92.4                | 21        |
| CaO/SiO$_2$      | 65              | 8:1         | 150        | 5                       | 93.4                | 37        |
| CaO/SiO$_2$      | 65              | 8:1         | 150        | 5                       | 93.8                | present work |

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Notes

The authors declare no competing financial interest.

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NOMENCLATURE

FAME, fatty acid methyl ester; %FAME, yield of fatty acid methyl ester; SBC, sludge biochar; A-SBC, activated sludge biochar; mCa/A-SBC-T, (m = 20, 30, 40%) calcium loaded A-SBC calcined at T (600, 700, 800 °C)

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