Enhancement of Biodiesel Production Via Sequential Esterification and Transesterification Over Solid Superacidic and Superbasic Catalysts

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ABSTRACT
Soybean oil containing a fatty free acid (FFA; palmitic acid, 5.0 wt%) was converted to biodiesel by a two-step process in a catalytic fixed-bed batch reactor using SO4²⁻/ZrO2/Al2O3, KF/CaO–Fe3O4, and Na/NaOH/Al2O3 catalysts. A solid superacidic (SO4²⁻/ZrO2/Al2O3: 0.1–1.5 M H2SO4) and two solid superbasic (KF/CaO–Fe3O4, 5–25 wt% KF; Na/NaOH/Al2O3, 10–25 wt% NaOH) catalysts were prepared by calcination at 300–700 °C and 200–700 °C, respectively. Notably, the FFA removal efficiency of SO4²⁻/ZrO2/Al2O3 (80.0%) was much higher than that of commercial Amberlyst IR 120 (30.0%) in a 3-h reaction. Optimal biodiesel yields were obtained using KF/CaO–Fe3O4 (83.0%) and Na/NaOH/Al2O3 (100.0%). Catalytic reaction mechanisms of the conversion of soybean oil with FFA into biodiesel using solid superacidic and superbasic catalysts were also proposed. The FFA and soybean oil were converted to biodiesel over the superacidic and superbasic catalysts, respectively.

Keywords
Solid superbasic/superacidic catalysts; Biodiesel; Esterification; Transesterification; Fatty free acid removal.

1. INTRODUCTION
Global warming and climate change are serious problems that threaten living beings worldwide. The shortage of and pollution resulting from traditional hydrocarbons fuels such as coal, gasoline, and natural gas has led to a demand for alternative fuels. Biodiesel, also known as fatty acid methyl esters (FAME), can be produced from energy crops such as soybean, sunflower, and rapeseed, and has become an ideal candidate for satisfying the global energy demand [1]. Furthermore, biodiesel is regarded as a green fuel due to its low emissions of nitrogen and sulfur compounds, making it much cleaner than fossil fuels. Some of the physical properties of biodiesel (flash point, 186 °C; cetane number, 51.2; oxygen content, 11.0%; heat value, 9.61 kcal kg⁻¹) are similar to those of fossil diesel (flash point, 52 °C; cetane number, 46.0; oxygen content, 0.6%; heat value, 10.84 kcal kg⁻¹) used in vehicles [2,3]. However, the flash point of biodiesel is much higher than that of fossil diesel, indicating that the storage and delivery of biodiesel is much safer than that of commercial diesel. In addition to biodiesels, more than 350 types of plant oils with excellent physical properties, including palm [2,4], peanut [2,5], soybean [4,6,7], rapeseed [4,8], sunflower [4,9], and cottonseed [10] oils, have been studied for direct use in diesel engines. Although plant oils can be used in biodiesel engines with many advantages, this could exacerbate food shortages. Therefore, recycling waste animal, plant, or cooking oils is a better option for biodiesel production [1,4,11–14]. Microwave [7,15], ultrasound-assisted [15], pyrolysis [6], supercritical extraction [8], microemulsion [15], and transesterification [10,11,16–20] methods have been reported for the preparation of biodiesel. However, these methods have many disadvantages for industrial applications. Similarly, pyrolysis requires huge amounts of energy and emits numerous toxic aromatic compounds [6]. Furthermore, microemulsified oils can easily contaminate diesel systems and cannot be stored long term. Therefore, transesterification is the most favorable method for biodiesel production.
To induce and accelerate the transesterification of oils, the addition of catalysts, including acidic, alkaline, heterogeneous, lipase, and homogeneous catalysts, is required [4,8,10,12,17,20–29]. Transesterification has been shown to be a three-step continuous reversible reaction [30]. In general, transesterification can be easily performed by reacting oils and methanol with alkali catalysts at 60 °C for 0.5 h. A high FAME content in oils can negatively influence the catalytic performance of alkali catalysts. For such FFA-rich oils, acidic catalysts can be used to catalyze the transesterification [30,31]. Furthermore, low-carbon alcohols such as methanol, ethanol, and 1-butonol are often added during the transesterification of energy crops and waste cooking oils to enhance the biodiesel yield. In terms of economic efficiency and environmental protection, the transesterification of waste oil feedstocks can afford high-quality biodiesel and produce less byproduct waste [31–32]. Notably, Benessere et al. [21] prepared a novel and robust Zn-based homogeneous catalyst (Zn(OAc)2(N,N'-chelate)) that repeatedly promoted the esterification and transesterification of vegetable oils at 160 °C in 2 h. A high FAME yield (94±2%) was obtained in the transesterification of soybean oil and methanol using Zn(OAc)2(N,N'-chelate) catalyst.

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Alkali catalysts are still widely used in oil transesterification due to their low price and superior catalytic performance. In general, transesterifications using alkali catalysts involve dissolving the catalyst, such as NaOH or NaOCH₃, in alcohols, to produce R'O⁻ ions (R’, alcohol alkyl group). These R'O⁻ ions break the C=O bonds of triglycerides (TG), forming tetrahedral intermediates that can react with alcohols continuously. Finally, another R'O⁻ ion and hydrated tetrahedral intermediate are formed, which rearrange to afford a FAME and diglyceride (DG). Unfortunately, undesired water, which can reduce the transesterification efficiency, can be produced during NaOH dissolution. Although water is not produced when using NaOCH₃, this catalyst is much more expensive than NaOH. Therefore, NaOH remains the most common alkali catalyst used in industry. Waste plant, animal, or cooking oils taken for use as feedstocks have high FFA and water contents that are unsuitable for transesterification. FFA can react with alkali catalysts to form fatty acid salts (soaps) via saponification. These soaps increase the viscosity of the reactants, which increases the cost of product separation. Meanwhile, water can hydrolyze TG to DG and FFA, with the formed FFA able to react repeatedly with the alkali catalyst for transesterification and saponification [1]. Therefore, to eliminate saponification, a two-stage transesterification method was proposed, wherein an acidic catalyst is first used to convert FFA into FAME, and then an alkali catalyst is used to complete the transesterification [28–32]. Jitputti et al. [36] used palm kernel and coconut oils as feedstocks and tested six solid transesterification catalysts to compare their catalytic performances and biodiesel yields. Among them, the heterogeneous catalyst SO₄²⁻/ZrO₂ showed the highest catalytic activity and prevented saponification. Unfortunately, the used SO₄²⁻/ZrO₂ catalyst could not be recycled in subsequent reactions due to a significant loss in catalytic activity. Previous studies reported about an acid catalyst that was used to reduce the FFA content in the oil to less than 2.0 wt%, and then transesterification of the refined oil was catalyzed by an alkali catalyst to obtain high-concentration biodiesels (91.0 wt%) [29]. Recently, superacidic solid sulfated metal oxide (SMO) catalysts have attracted much attention due to their extremely high alkane isomerization efficiency and facile fabrication [22,36]. These catalysts have generally been applied to alkane isomerizations, including butane/pentane isomerization, isobutane/1-butene alkylation, benzoic acid/methanol esterification, and octane cracking [1,10,32]. These alkane isomerizations can easily be induced using SMOs with high contents of superacidic sites [1,29]. Superacidic/Superbasic catalysts were proposed to help elucidate the catalytic behaviors of these as-synthesized catalysts under different synthesis conditions.

2. EXPERIMENTAL

2.1 Preparation of Solid Superacidic SO₄²⁻/ZrO₂/Al₂O₃

A mixture of ZrO₂ and Al₂O₃ powders (1.0 g, ZrO₂/Al₂O₃ = 1:1, w/w) was immersed in 0.1, 0.3, 0.5, 1.0, and 1.5 M H₂SO₄ aqueous solutions (15 mL), respectively, filtered, and dried at 160 °C overnight. A white solid superacidic SO₄²⁻/ZrO₂/Al₂O₃ (SZA) powder was obtained after calcination in an air stream (20 cm³ min⁻¹) at 200, 300, 329, 400, 500, 600, or 700 °C for 3 h. The SO₄²⁻/ZrO₂/Al₂O₃ samples prepared using different H₂SO₄ concentrations and calcination temperatures were denoted as SZA-a and SZA-b, respectively (a= 0.1, 0.3, 0.5, 1.0, and 1.5 M; b= 200, 329, 400, 500, 600, and 700 °C).

2.2 Preparation of Solid Superbasic KF/Fe₃O₄ and Na/NaOH/Al₂O₃

The KF/Fe₃O₄ (KFC) catalysts were prepared by loading 5, 10, 15, 20, or 25 wt% KF into a mixture of Fe₃O₄ (5.0 g) and CaO powders (20.0 g) in a KF aqueous solution for 2 h. The solid particles were filtered and dried at 105 °C for 24 h to remove water. The dried KF powder was calcined at 200, 329, 400, 600, or 700 °C. The KFC catalysts were prepared using different KF loadings and calcination temperatures were labeled as KFC-c and KFC-d, respectively (c= 5, 10, 15, 20, and 25 wt%; d= 200, 329, 400, 500, 600, and 700 °C). Another catalyst Na/NaOH/Al₂O₃ (NNA) was fabricated using a solid-phase reaction at high temperatures in a water-free environment. A γ-Al₂O₃ powder (15.0 g) was heated to 500 °C under a flowing nitrogen stream for 1 h. Subsequently, 13.0 wt% Na particles were added to the melted γ-Al₂O₃ (~2072 °C) with stirring under a nitrogen atmosphere at the melting temperature of NaOH (320 °C) for 2 h. Finally, 10, 15, 20, or 25 wt% of NaOH particles were individually added to the melted mixtures to achieve a good dispersion before cooling to 25 °C within 1 h under a flowing nitrogen stream. NNA catalysts with various NaOH weight percentages were obtained, denoted as NNA-e (e= 10, 15, 20, and 25 wt%).

2.3. Characterization of Solid Superacidic/Superbasic Catalysts

X-ray diffraction (XRD) patterns of the catalyst samples were recorded at a scan rate of 4° (2θ) min⁻¹ using monochromatic Cu Kα radiation (MAC Science, MXP18) at 30 kV and 20 mA. The recorded specific peak intensity and 2θ values were further

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identified with reference to a database system (JCPDS). The morphology, microstructure, and particle size of the solid superacidic/superbasic catalysts were investigated using field-emission scanning electron microscopy (FE–SEM; Hitachi, S-4700 Type II) and high-resolution transmission electron microscopy (HRTEM; Hitachi H–7500). The specific surface area and pore diameter were obtained from nitrogen adsorption–desorption isotherms (Micromeritics ASAP 2020) using the Brunauer– Emmett–Teller (BET) equation. The chemical composition on the surface of the solid superacidic/superbasic catalysts was determined by X-ray photoelectron spectroscopy (XPS, Physical Electronic ESCA PHI 1600) at the excitation energy of Al Kα (1486.6 eV). The C 1s (284.5 eV) peak was used as the calibration standard for wide-region spectra of aluminum, sulfur, zirconium, calcium, iron, and potassium species. XPS signals for the above species were recorded using a cylindrical mirror analyzer (CMA). The crystal structures of these as-prepared solid superacidic/superbasic catalysts were analyzed using Raman spectroscopy (HORIBA, iHR550).

The acidity and basicity of the solid superacidic/superbasic catalysts were measured using Hammett indicators. Two Hammett indicators with specific concentrations (anthraquinone, 9.6×10⁻⁷ M; p-nitrotoluene, 0.03 M) were prepared by mixing anthraquinone (0.05 g) or p-nitrotoluene (0.1 g) with toluene (25 mL) to measure the SZA acidity. Well-dried SZA particles (2.0 g) were mixed with these three Hammett indicators (1.2 mL) and the color changes recorded. In terms of KCF and NNA catalysts, three Hammett indicators (phenolthalain, 2.4-dinitroaniline, 4-nitroaniline) at 0.1 wt% were prepared by mixing 0.01 g phenolthalain, 2.4-dinitroaniline, or 4-nitroaniline with methanol (10 mL) for basicity measurements. KCF or NNA particles (0.1 g) were mixed with several drops of the Hammett indicators, and benzoic acid/methanol solution (1:1, v/v) was added until the catalyst surface color changed from purple to white. The amount of benzoic acid/methanol solution consumed was recorded to calculate the KCF and NNA basicity.

X-ray absorption near edge structure (XANES)/extended X-ray absorption fine structure (EXAFS) spectra were collected on Wiggler beamlines 16A1 and 01C1 at the National Synchrotron Radiation and Research Center (NSRRC) of Taiwan. The electron storage ring was operated at an energy of 1.5 GeV and a ring current of 100–200 mA. Data were collected in transmission mode using a Lytle detector in the region of the Zr L₂,3-edge at 25 °C and subsequently normalized using Athena (vi) software, with the linear pre-edge and polynomial post-edge backgrounds subtracted from the raw ln(I/I₀) data (where I₀ is the light intensity after passing through the sample and I₀ is the initial light intensity), and then analyzed using Artemis (vi) software with FFED code-8 [25–30]. Spectra were first energy-calibrated by simultaneously recording the transmission spectra of the Zr and Fe foils with Athena (vi), in which the energies of the first inflection points in the reference sample absorption edges were defined as 2307 and 7112 eV, respectively. After calibration, the samples were background-corrected (using a linear pre-edge region and a polynomial for the post-edge region) and normalized. EXAFS energy spectra were then converted into wavevector K-space form. The data directly reflected the average local environment around the absorbing atoms. The spectra were analyzed using the IFEFFIT software package. The theoretical paths for the Zr–O and Fe–O species were generated using the FEFF-8 program based on crystallographic data of the individual species and used to fit the first coordination shell of the experimental data. The coordination number, interatomic distance, Debye–Waller factor, and inner potential corrections were used as variables for the fitting procedures.

2.4. Free Fatty Acid Removal and Biodiesel Productions Using Solid Superacidic/Superbasic Catalysts Via Esterification and Transesterification

Soybean oil underwent transesterification using an emulsifying machine (IKA, T25 digital) equipped with a stirrer (IKA, S25N–25G) and a stationary column (with side-holes of 2-mm diameter) packed with catalyst. Before transesterification, the 200-mL mixture of soybean oil (purchased from Uni-President Inc.) and methanol (20:1, v/v) was poured into a flask, and heated to 60 °C with mild stirring at 600 rpm. Solid superacidic or superbasic catalyst particles (5.0 wt%) were filled in the stationary column as the catalyst and submerged into the mixture with vigorous stirring using an emulsifying machine for 2 h. Subsequently, the emulsified mixture was cooled in 2 min, and the clear upper liquid was separated from the mixture by centrifugation (Unico, Powerspin HX model) at 3400 rpm for 30 min. Finally, per milliliter acetone was mixed with the separated liquid (20 mL) to extract biodiesel. The concentration calibration curves of each species in the as-prepared biodiesel were analyzed by GC-MS (mass spectrometry, Agilent, HP 6890). During GC-MS analysis, the liquid mixture (0.5 mL) was injected into the GC column (Porapak Q stainless-steel column, 80/100) with a flame ionization detector (FID) at 10 mL min⁻¹ with a flowing H₂ stream. To acquire the FFA efficiency of solid superacidic catalysts, palmitic acid was added into soybean oil to compose a mixture with 5.0 wt% palmitic acid. The palmitic acid could be converted into methyl palmitate via esterification using 5.0 wt% SZA serial catalysts in the emulsifying machine. Therefore, FFA removal was calculated using Eq. (1) and compared with that using two commercial catalysts, namely Amberlyst 15 and Amberlyst IR120 (purchased from Sigma–Aldrich Inc.).

\[
\text{Free fatty acid removal (\%)} = \frac{W_a - W_t}{W_a} \times 100\%
\]

where \( W_a \) is the initial weight of palmitic acid (g), and \( W_t \) is the weight of residual palmitic acid after esterification (g)

The biodiesel (alkyl ester) yields using 5 wt% solid superbasic catalysts were evaluated according to the following assumptions: (i) The dominant species in soybean oil were triglycerides; (ii) the weight of the biodiesel product was equal to that of soybean oil. The biodiesel yield was calculated using Eq. (2).

\[
\text{Yield of biodiesel (\%)} = \frac{W_{\text{actual}}}{W_{\text{theoretical}}} \times 100\% = \frac{W_{\text{actual}}}{W_{\text{theoretical}}} \times 100\% = \frac{W_{\text{actual}}}{W_{\text{theoretical}}} \times 100\% = \frac{W_{\text{actual}}}{W_{\text{theoretical}}} \times 100\% = \frac{W_{\text{actual}}}{W_{\text{theoretical}}} \times 100\% = \frac{W_{\text{actual}}}{W_{\text{theoretical}}} \times 100\%
\]

where \( W_{\text{actual}} \) is the actual weight of produced alkyl esters (g), \( W_{\text{theoretical}} \) is the theoretical weight of alkyl esters after complete reaction (g), \( C_{\text{ester}} \) is the sum of the concentrations of various alkyl esters (ppm or mg L⁻¹), \( n \) is the dilution coefficient, \( V_{\text{total}} \) is the total liquid volume (mL), \( W_{\text{oil}} \) is the mass of the soybean oil (g), and \( F_{\text{TG}} \) is the weight fraction of triglycerides in soybean oil (wt%).

3. RESULTS AND DISCUSSION

3.1 Crystal Structures and Morphologies of Catalysts

The crystal structures of the as-prepared solid superacidic and superbasic catalysts were characterized using XRD patterns, as shown in Figs. 1(a)–(c). Characteristic peaks of tetragonal-ZrO₂ (T-ZrO₂; 20 = 31.6°, 34.2°, 35.2°, 50.2°, and 57.6°), monoclinic-ZrO₂...
calcination temperatures. The crystal structure of the solid
became covered with KF, CaO, or Ca(OH)\(_2\) through magnetic
attraction to form several bulk structures. The longer calcination
time likely resulted in the deposition of KF, CaO, or Ca(OH)\(_2\),
which increased the particle sizes of the KF catalyst. Figures 2(e)
and 2(f) show that the morphology NNA catalyst was a flat plane
with some particles on the surface. This flat plane formed on NNA
catalysts because they were dissolved due to the facile absorption
of moisture from the atmosphere, which resulted from their high
hygroscopicity. Furthermore, lattice spaces (d) and Miller indexes
(hkl) of each species in the as-prepared solid superacidic and
superbasic catalysts were confirmed using HRTEM images, as
shown in Figs. 3(a)–(f). In Figs. 3(a) and 3(b), the Miller index
(111) and lattice spacing of 0.32 nm showed that ZrO\(_2\) was present,
which was consistent with the XRD results. Furthermore, bulk
particles of KCF catalyst were observed as tiny black spots covered
with a large translucent bulk, as shown in Fig. 3(c). In Fig. 3(d),
the lattice spacing (d = 0.17 nm) and Miller index (101) of these black
spots showed that they might be Fe\(_3\)O\(_4\) particles. This was
consistent with the FE-SEM observations. However, the lattice
space and Miller index of NNA catalyst were not identified, with
only a bulk of aggregated particles with a diameter of 8–11 nm
recognized, as shown in Figs. 3(e) and 3(f).

A solid superacidic catalyst KF/CaO-Fe\(_3\)O\(_4\) (KCF) was also
investigated by XRD, as shown in Fig. 1(b). The intensities of the
characteristic peaks of KCaCO\(_3\)F (2\(\theta\) = 20.1\(^\circ\), 35.2\(^\circ\), and 45.9\(^\circ\))
decreased with increasing calcination temperature. In contrast, the
characteristic peaks of Ca(OH)\(_2\) (2\(\theta\) = 18.1\(^\circ\) and 28.9\(^\circ\)), CaO (2\(\theta\) =
32.4\(^\circ\), 37.5\(^\circ\), 54.0\(^\circ\), 64.3\(^\circ\), and 67.5\(^\circ\)), Fe\(_3\)O\(_4\) (2\(\theta\) = 44.7\(^\circ\)
and 51.0\(^\circ\)), and KCF (2\(\theta\) = 41.3\(^\circ\)) in KCF were more intense after calcination
at 600 and 700 \(^\circ\)C than at 200–400 \(^\circ\)C. It is known that KCaCO\(_3\)F
may weaken the physical strength of the KCF catalyst. Therefore,
KCaF\(_3\) production was more favorable in the calcination step of
the KCF catalyst. Among all calcination temperatures, the highest
proportion of KCaF\(_3\) in KCF appeared at 329 \(^\circ\)C, which resulted in
the highest physical strength compared with those at other
calcination temperatures. The crystal structure of the solid
superbasic catalyst, Na/NaOH/Al\(_2\)O\(_3\) (NNA), was also confirmed by
XRD, as shown in Fig. 1(c). In addition to characteristic peaks of
NaOH (2\(\theta\) = 46.3\(^\circ\), 50.3\(^\circ\), 61.7\(^\circ\), 76.4\(^\circ\)), and 78.3\(^\circ\)), characteristic peaks of NaAlO\(_2\) (2\(\theta\) =
21.8\(^\circ\), 30.2\(^\circ\), 31.7\(^\circ\), 40.1\(^\circ\), and 40.2\(^\circ\)) and Al(OH)\(_3\) (2\(\theta\) = 43.6\(^\circ\), 66.5\(^\circ\), and 72.5\(^\circ\))
were identified in the XRD, which indicated NaAlO\(_2\) formation
(Al\(_2\)O\(_3\) + 2NaOH → 2NaAlO\(_2\) + H\(_2\)O). Furthermore, hydrogen
gas may also be formed during calcination (Na\(_2\)H\(_2\)O → 2NaOH + H\(_2\)). These intrinsic interactions of NNA may be due to
the strong hygroscopicity of Na and NaOH resulting in the
instability of the NNA structure. The morphologies of the SZA,
KCF, and NNA catalysts were observed using FE-SEM, as shown in
Figs. 2(a)–(f). Interestingly, Figs. 2(a) and 2(b) show that the
H\(_2\)SO\(_4\) concentration used during preparation significantly affected
the morphology of the SZA catalyst. At low (0.1 M) and high (1.5 M)
H\(_2\)SO\(_4\) concentrations, the SZA morphologies were tetragonal
and monoclinic, with particle sizes of 3.8 and 7.5 \(\mu\)m, respectively.
As shown in Figs. 2(c) and 2(d), the morphologies of the KCF
catalysts calcined for short (3.0 h) and long (5.0 h) periods showed
aggregated particles. This implied that the magnetic Fe\(_3\)O\(_4\) particles
became covered with KF, CaO, or Ca(OH)\(_2\) through magnetic
attraction to form several bulk structures. The longer calcination
time likely resulted in the deposition of KF, CaO, or Ca(OH)\(_2\),
which increased the particle sizes of the KF catalyst. Figures 2(e)
and 2(f) show that the morphology NNA catalyst was a flat plane

<p>| Table 1. Pore textural properties of SO(_4)(^2-)/ZrO(_2)/Al(_2)O(_3), KF/CaO-Fe(_3)O(_4), and Na/NaOH/Al(_2)O(_3). |
|-------------------------------------------------|------------------|------------------|------------------|</p>
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Langmuir/BET surface area (m(^2)g(^{-1}))</th>
<th>Pore volume (cm(^3)g(^{-1}))</th>
<th>Pore size distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO(_4)(^2-)/ZrO(_2)/Al(_2)O(_3)</td>
<td>1.17±1.1</td>
<td>1.47±1.0(^2)</td>
<td>97.0 ± 3.0</td>
</tr>
<tr>
<td>KF/CaO-Fe(_3)O(_4)</td>
<td>151.5 ± 96.0</td>
<td>0.02</td>
<td>95.0 ± 3.0</td>
</tr>
<tr>
<td>Na/NaOH/Al(_2)O(_3)</td>
<td>199.8 ± 71.9</td>
<td>0.15</td>
<td>97.0 ± 3.0</td>
</tr>
</tbody>
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\(^2\) Pore volume and pore size distribution were measured by 
IUH method.

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3.3. Surface Chemical Compositions of Catalysts

Figures 5(a)–(f) show the chemical species and compositions on the SZA and KCF catalyst surfaces. The Al species in SZA were identified as Al₂O₃ with two different electronic orbitals, 2p₁/₂ and 2p₃/₂, which might indicate that the bonding strength of Al₂O₃ was weak in the calcination procedure, as shown in Fig. 5(a). Similarly, Figs. 5(b) and 5(c) indicate that only single S and Zr species were detected by XPS spectra of S 2p and Zr 3d elements, respectively. For SZA, SO₄²⁻ from the addition of H₂SO₄ did not participate in SZA crystal formation, but still formed Al₂(SO₄)₃ on the SZA surface. The chemical species on the KCF surface were also analyzed. As shown in Fig. 5(d), the existence of several Ca species, including CaCO₃, CaO, KCaF₃, and KCaO₃, was confirmed, in agreement with their XRD patterns. CaCO₃ was probably formed due to partial carbonation of CaO when exposed to the atmosphere. Figure 5(e) shows that Fe species on the KCF surface are K₂FeO₄ and Fe₃O₄. Regarding valence, Fe₃O₄ is a unique iron oxide with a non-integer iron valence, which can also be expressed as Fe₂O₃•FeO. Therefore, the two Fe species peaks were probably due to the mixed iron valence of Fe₂O₃. Similarly, the K species on the KCF surface were identified as KCaF₃ and KF, as shown in Fig. 5(f).

3.4. Oxidation States and Fine Structures of Catalysts

Two absorption peaks (L₂ and L₃-edges) were present in the Zr XANES spectrum at 2225.8 and 2315.4 eV, as shown in Figs. 6(a) and 6(b), showing the existence of Zr species.

Owing to the variety of Fe atoms in KCF, the Fe valence was compared with other iron standards, such as Fe foil, FeO, Fe₂O₃, and Fe₃O₄, as shown in Figs. 6(c) and 6(d). The absorption peak of KCF at 7127.3 eV overlapped with that of Fe₃O₄, indicating that the Fe valence in KCF was similar to that of Fe₂O₃. This result was consistent with the XPS spectra of KCF. Structural investigations of Zr and Fe atoms in SZA and KCF catalysts were performed using EXAFS, which confirmed the existence of Zr–O and Fe–O bonds, as shown in Figs. 7(a) and 7(b), respectively. Table 2 shows the fine structural parameters of Zr/Fe standards, SZA, and KCF. Zr and Fe evidently existed as Zr²⁺ and Fe⁸/₃⁺, as compared with known standards. Interestingly, the Fe valence in KCF was found to be a Fe₂O₃•FeO mixture.
Fig. 6. Normalized XANES/first-order derivatives spectra of (a) Zr in SO$_4^{2-}$/ZrO$_2$/Al$_2$O$_3$, and (c) Fe in KF/CaO–Fe$_3$O$_4$ and iron standards.

Fig. 7. Fourier transformed EXAFS spectra of (a) Zr in SO$_4^{2-}$/ZrO$_2$/Al$_2$O$_3$ and (b) Fe in KF/CaO–Fe$_3$O$_4$.

To confirm the XRD results, the crystal structures of SZA and KCF were also investigated using Raman spectroscopy, as shown in Figs. 8(a) and 8(b). Figure 8(a) shows sharp peaks for T-ZrO$_2$ (270, 315, 455, 602, and 645 cm$^{-1}$) and M-ZrO$_2$ (398, 577, and 797 cm$^{-1}$). This indicated that T-ZrO$_2$ was the dominant species for the efficient removal of FFA, which was consistent with the earlier XRD results. Furthermore, the peaks of Al$_2$O$_3$ and SO$_4^{2-}$ were likely contributed by added Al$_2$O$_3$ and residual H$_2$SO$_4$ during SZA preparation. As shown in Fig. 8(b), the baseline of the KCF spectrum was not horizontal because KCaF$_3$ was present, which can form a volcano-shaped spectrum. KF, CaO, and Fe$_3$O$_4$ were also confirmed to be present in the KCF spectrum by comparison with standard spectra.

3.5. Acidic Strengths, FFA Removal Efficiencies, and Biodiesel Yields of Catalysts

The acidic strengths of SZA catalysts prepared using various H$_2$SO$_4$ concentrations and calcination temperatures were measured using Hammett indicators, as shown in Table 3.

The SZA acidic strengths increased with H$_2$SO$_4$ concentration until the maximum value was achieved.

Fig. 8. Raman spectra of (a) SO$_4^{2-}$/ZrO$_2$/Al$_2$O$_3$ and (b) KF/CaO–Fe$_3$O$_4$.

Accordingly, measurements of SZA catalysts were repeated with different weights of ZrO$_2$ and Al$_2$O$_3$ to confirm the actual active component in SZA catalyst. Different weights of ZrO$_2$ and Al$_2$O$_3$ did not change the colors of the Hammett indicators. This showed that H$_2$SO$_4$ was the main active acidic component for biodiesel production. Furthermore, the colors of the two Hammett indicators were almost identical for SZA catalysts calcined at different temperatures. Similar measurements were also applied to KCF and NNA catalysts, as shown in Table 4. The amounts of KF and NNA added were found to be proportional to the basic strengths due to color changes of the Hammett indicators. These color changes showed that the basic strengths of KCF and NNA catalysts reached H$_v = 15$ and 18, respectively.

The FFA removal efficiencies of commercial (Amberlyst IR 120 and Amberlyst 15) and SZA catalysts prepared at different H$_2$SO$_4$ concentrations and calcination temperatures are shown in Figs. 9(a)–(c). During 3-h reactions, the FFA removal efficiencies were in the order Amberlyst 15 (98.0%) > SZA (80.0%) > Amberlyst IR 120 (30.0%), which showed the potential of SZA for application in waste oil transesterification (Fig. 9(a)). The effect of H$_2$SO$_4$ concentration on the FFA removal efficiency of SZA is shown in Fig. 9(b). The FFA removal efficiency was proportional to the H$_2$SO$_4$ concentration, with an optimal concentration of 1.0 M, which suggested that SO$_4^{2-}$ was the effective active site for transesterification. However, the FFA removal efficiency of SZA was not further enhanced by adding higher concentrations of H$_2$SO$_4$ (1.5 M) to SZA preparation. This might be due to the empty intramolecular spaces in the SZA catalyst being saturated and occupied by the SO$_4^{2-}$ from H$_2$SO$_4$(aq) dissociation. Furthermore, the effect of calcination temperature on the FFA removal efficiency of SZA is shown in Fig. 9(c).
Interestingly, the FFA removal efficiency initially increased with increasing calcination temperature, but then decreased at 700 and 800 °C. This indicated that the ZrO$_2$ crystal structure transformed from T-ZrO$_2$ to M-ZrO$_2$ at high calcination temperatures, which reduced the catalytic activity of SZA for FFA removal.

3.6. Mechanisms of FFA Esterification and Soybean Oil Transesterification

In the present work, FFA esterification and soybean oil transesterification were conducted using solid superacidic and superbasic catalysts, respectively. The related catalytic mechanisms are proposed in Figs. 11(a) and 11(b). The mechanism of palmitic acid esterification is simple, as shown in Fig. 11(a). According to the literature [30,31,32], biodiesel could be produced from excess FFA in oils via esterification using SMOs, such as SO$_4$–ZrO$_2$. In this work, intramolecular bonds of palmitic acid (O–H) and methanol (C–O) were previously cracked into palmitic acid groups (CH$_3$(CH$_2$)$_{14}$COO–), hydronium ions (H$_3$O$^+$), methyl groups (CH$_3$–), and hydroxy groups (–OH) at superacidic active sites over SZA surfaces. Subsequently, CH$_3$(CH$_2$)$_{14}$COO– groups bond with CH$_3$– groups, forming a long-chain methyl hexadecanoate (known as biodiesel). Moreover, water was also formed as a by-product from the combination of H$^+$ and OH$^−$. The esterification reaction was terminated when palmitic acid was completely consumed. Conversely, the transesterification of soybean oil using solid superbasic catalysts is more complex than the esterification of palmitic acid. This might be due to the multicomponent methyl esters present in soybean oil, including methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate. Figure 11(a) shows the mechanism of a chain transesterification reaction using a solid superbasic catalyst. Before transesterification of the soybean oil, methanol was first converted into the required methoxide ion (CH$_3$O–) and water in the basic solution (step 1). When the methyl ester groups contacted with these CH$_3$O– ions, the C=O bonds were broken, temporarily forming tetrahedral methyl intermediates (step 2). Subsequently, these tetrahedral intermediates continuously react with methanol, producing CH$_3$O– and protonated tetrahedral methyl intermediates (step 3). Finally, these protonated tetrahedral methyl intermediates are reinserted into FAME and methoxymethanediol (CH(OH)$_2$OCH$_3$; step 4).

Fig. 11. Reaction mechanisms of (a) palmitic acid (FFA) esterification and (b) soybean oil transesterification for biodiesel production using solid superacidic (SO$_4$$_2$/ZrO$_2$/Al$_2$O$_3$) and solid superbasic (KF/CaO–Fe$_3$O$_4$ and Na/NaOH/Al$_2$O$_3$) catalysts, respectively (R: hydrocarbon groups of methyl esters in soybean oil).

As shown in Figs. 10(a)–(c), the biodiesel yields of two superbasic catalysts were also investigated. Figure 10(a) shows that the biodiesel yield of NNA was much higher than that of KFC after 1 h, due to the stronger basicity. Generally, catalysts with stronger basicity give higher biodiesel yields with faster transesterification. To enhance the biodiesel yield of KCF, the KF loading amounts and calcination temperatures were investigated. The effect of KF loading amount on the biodiesel yield of KCF is shown in Fig. 10(b). The biodiesel yield increased to a maximum (83.0%) at 25 wt% KF, and then decreased for higher amounts of KF. This was attributed to excess KF covering the active sites for transesterification. The effect of calcination temperature on the biodiesel yield of KCF is shown in Fig. 10(c). Similarly, the biodiesel yield of KCF increased with increasing calcination temperature up to 600 °C due to the appearance of new active sites during calcination via crystal transformation at high temperatures. Although 329 °C was the optimal calcination temperature for stabilizing the KCF structure, the biodiesel yield was not the highest observed. Therefore, the optimal calcination temperature for KCF with the highest biodiesel yield was 600 °C. At calcination temperatures exceeding 600 °C, catalyst sintering causes a decrease in active sites and biodiesel yield.

Fig. 10. Biodiesel yields of KF/CaO–Fe$_3$O$_4$ (a) and Na/NaOH/Al$_2$O$_3$, (b) with different KF loading, and (c) calcined at 200–700 °C.
4. CONCLUSIONS

In this study, a solid superacidic (SO\(_4^{2-}/\)ZrO\(_2/\)Al\(_2\)O\(_3\)) and two solid superbasic (KF/Fe\(_3\)O\(_4/\)CaO and Na/NaOH/Al\(_2\)O\(_3\)) catalysts were successfully prepared using various reactant ratios and calcination temperatures. In particular, the FFA removal percentage of SO\(_4^{2-}/\)ZrO\(_2/\)Al\(_2\)O\(_3\) (80.0%) was higher than that of commercial Amberlyst IR 120 (30.0%). Furthermore, the highest biodiesel yields were acquired in 3-h transesterification reactions using KF/Fe\(_3\)O\(_4/\)CaO and Na/NaOH/Al\(_2\)O\(_3\) (100.0%). From the proposed catalytic reaction mechanisms, FFA and soybean oil were converted to biodiesels over superacidic and superbasic catalysts, respectively. These results indicate that waste oils with FFA can be efficiently converted to biodiesel.

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6. REFERENCES