



One-step production of biodiesel from oils with high acid value by activated Mg–Al hydrotalcite nanoparticles



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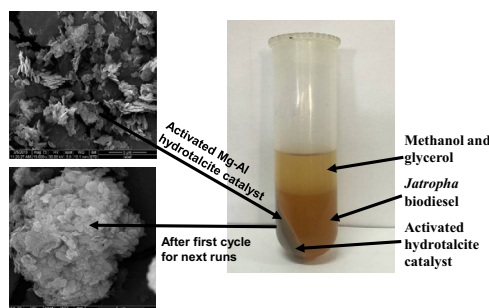
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HIGHLIGHTS

- Activated Mg–Al hydrotalcite (HT-Ca) nanoparticles (<45 nm) were synthesized.
- HT-Ca presented both acidic and basic for high acid value oils.
- Mg₄Al₂(OH)₁₄·3H₂O, Mg₂Al(OH)₇ and AlO(OH) as active composites.
- 93.4% & 92.9% biodiesel yield at AV of 6.3 & 12.1 mg KOH/g.
- 4 cycles with *Jatropha* biodiesel yield >86% at AV of 6.3.

GRAPHICAL ABSTRACT

Activated Mg–Al hydrotalcite nanoparticles (<45 nm) were synthesized. The catalyst presented both acidic and basic to produce biodiesel from oils with high acid value (AV). Biodiesel yield reached 93.4% and 92.9% from *Jatropha* and soybean oils with AV of 6.3 and 12.1 mg KOH/g. The catalyst can recycle 4 times with *Jatropha* biodiesel yield >86%.



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ABSTRACT

Activated Mg–Al hydrotalcite (HT-Ca) nanoparticles (<45 nm) were synthesized by co-precipitation and hydrothermal activation with aqueous Ca(OH)₂ solution. They were characterized by various techniques including X-ray diffraction, inductively coupled plasma atomic-emission spectrometer, Brunauer–Emmett–Teller method, scanning electronic microscope-X-ray energy dispersive analysis and temperature programmed desorption method. HT-Ca presented both acidic and basic due to the formation of Mg₄Al₂(OH)₁₄·3H₂O, Mg₂Al(OH)₇ and AlO(OH) nanocrystals to esterify and transesterify oils with high acid value (AV). Under conditions of 5 wt% HT-Ca, 160 °C, 30/1 methanol/oil molar ratio and 4 h, 93.4% *Jatropha* biodiesel yield was obtained at AV of 6.3 mg KOH/g with 4 cycles (biodiesel yield > 86%). It was further found that it can resist free fatty acids, and biodiesel yield reached 92.9% from soybean oil with high AV of 12.1. HT-Ca catalyst showed a potential practical application for direct production of biodiesel from oils with high AV without pretreatment.

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1. Introduction

Due to the depletion of fossil fuels and global warming, biodiesel research has received significant attention in the past few decades (Lu et al., 2015; Sankaranarayanan et al., 2012; Gui et al., 2008). Biodiesel produced from edible and non-edible oils, such as animal fats, cooking oil, algae oil and microbial lipids by transesterification process is considered as an environmental friendly replacement for conventional diesel because it is clean, non-toxic, renewable and carbon neutral (Ramadhas et al., 2005; Chen et al., 2012; Thanh et al., 2010; Luu et al., 2014; Teo et al., 2014; Macor and Pavanello, 2009). Basic catalytic transesterification of oils with homogeneous [e.g., sodium methoxide, potassium or sodium hydroxide (Luque et al., 2010)] and heterogeneous catalysts [e.g., CaO (Lin et al., 2012), sodium silicate (Guo et al., 2010; Zhang et al., 2015)] is the most common method at low temperatures (e.g., 50–60 °C). Solid catalysts are widely studied for biodiesel production because they are recyclable (Singh Chouhan and Sarma, 2011). For example, calcined layered double hydroxides (LDHs) as base heterogeneous catalysts have gained the awareness because of their high activity for biodiesel production (Shumaker et al., 2008; Deng et al., 2011; Barakos et al., 2008). However, basic catalysts are easily to form soap with free fatty acids (FFAs) when low qualified oils with high acid value (AV) are used as raw materials, and two-step process composed of esterification and transesterification catalyzed over acidic and basic catalysts was developed (Deng et al., 2010, 2011). But, the process is too complex and costly.

Therefore, solid acid catalysts are synthesized for one-step production of biodiesel directly from oils with high AV since acid can catalyze both esterification and transesterification (Dawodu et al., 2014; Shu et al., 2010; Zhang et al., 2014). However, acid-catalyzed transesterification requires harsh conditions, such as 220 °C for 4.5 h (Shu et al., 2010). Hydrotalcites (a group of LDHs) present both acidic and basic properties that can promote reactions of esterification by acidic sites and transesterification mainly by basic sites at lower temperatures to avoid saponification of FFAs. Catalytic activity of hydrotalcites can be further enhanced with modifications such as activation with saturated aqueous Ca(OH)₂ solution (Fang et al., 2011).

This work aims to directly produce biodiesel from oils with high acid value using prepared activated nanosized Mg–Al hydrotalcite. Reaction conditions are optimized by single-factor experiments. Catalysts are characterized by various techniques before and after biodiesel production.

2. Experimental

2.1. Materials

Analytical reagents Mg(NO₃)₂·6H₂O (≥99.0%), Al(NO₃)₃·9H₂O (≥99.0%), Ca(OH)₂ (≥95.0%), CaCO₃ (≥99.0%), dehydrated methanol (≥99.5%), urea (≥99.0%), dichloromethane (≥99.0%) and oleic acid (about 80% purity) were purchased from Xilong Chemical Factory Co., Ltd. (Shantou, Guangdong). Standard methyl esters of [palmitate (C_{16:0}), linolenate (C_{16:1}), stearate (C_{18:0}), oleate (C_{18:1}), linoleate (C_{18:2}), linolenate (C_{18:3}) and heptadecanoic acid] with purity ≥99% were obtained from Sigma (Shanghai). Soybean oil (AV of 0.7 mg KOH/g, molecular weight of 881.2 g/mol) was bought from a supermarket (Carrefour) in Kunming, and it was blended with oleic acid to achieve different AV (0.7, 6.8, 12.1, 18.1 and 22.1 mg KOH/g with their corresponding molecular weights of 881.2, 881.1, 866.2, 863.1 and 859.6 g/mol) for experiments. *Jatropha* oils (AV of 6.3, 12.8 and 17.2 mg KOH/g with molecular weights of 862.2, 858.7 and 860.0 g/mol, respectively) were

obtained from Yunnan Shenyu New Energy Co., Ltd. and Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences, respectively.

2.2. Catalyst preparation

Similar to previous method (Fang et al., 2011), 0.2 M Mg(NO₃)₂·6H₂O, 0.1 M Al(NO₃)₃·9H₂O, 1.5 M solid urea and 300 mL deionized water were loaded in a 500 mL beaker in water bath at room temperature in an ultrasonic cleaner for dissolution. The aqueous solution was transferred into a 500 mL three-neck flask with a water-cooled condenser in an oil bath at 105 °C with vigorous stirring for 12 h, and settled at 95 °C for 12 h. The precipitates together with their mother solution were transferred into a conical beaker (1 L), and washed for 8 times with deionized water to remove residual urea until the pH of supernatant reached about 7. The product was filtered, freezing dried (PDU-1200, EYELA, Tokyo Rikakikai Co., Ltd.) and identified as Mg–Al hydrotalcite (HT). The HT powders (5 g) and saturated aqueous Ca(OH)₂ solution (250 mL) were put in a 300 mL autoclave (FCFD05-30, Jianbang Chemical Mechanical Co., Ltd., Yantai, Shandong) with mechanical agitation (500 rpm) at 150 °C for 10 h, and 200 °C for 1 h activation. The sample was washed with deionized water until neutral, and filtered (pore size 1–3 μm) then dried at 105 °C (WFO-710, EYELA, Tokyo Rikakikai Co., Ltd.) overnight. After ground and passed through 200 mesh sieve, activated Mg–Al catalyst was obtained and identified as hydrotalcite-calcium (HT-Ca). Some of Mg–Al HT powders were thermo-pretreated by heating to 300, 400 and 500 °C (at 5 °C/min heating rate) for 2 h calcination with N₂ flowing in a tubular furnace (SGL-1100, Shanghai Daheng Optics and Fine Mechanics Co., Ltd.) to remove carbonate for better subsequent activation. After similar activation, catalysts were obtained and named as HT300-Ca, HT400-Ca and HT500-Ca (300, 400 and 500 are calcination temperatures), respectively.

2.3. Catalyst characterization

Activated hydrotalcite-calcium (HT-Ca) was characterized by X-ray diffraction (XRD, Rigaku Rotaflex RAD-C, Tokyo) using a CuKα radiation (40 kV and 200 mA). The morphology and chemical element of HT-Ca and HT-Ca₁ (HT-Ca after 1 cycle) were examined with scanning electronic microscope-X-ray energy dispersive analysis (SEM-EDX; Quanta 200, FEI, Hillsboro, OR). The surface area and pore volume of catalysts were analyzed by Brunauer–Emmett–Teller method (BET, Tristar II 3020, Micromeritics Instruments, Atlanta, GA) with N₂ adsorption. Elemental compositions of catalysts after dissolution in water (about 25 mg catalyst dissolved in 10–15 mL 37% HCl, and diluted to 250 mL by deionized water) were determined by inductively coupled plasma atomic-emission spectrometer (ICP-AES, iCAP6300, Thermo Fisher Scientific, Waltham, MA). Basicity and acidity of catalysts were determined by temperature programmed desorption (TPD; Chemisorption analyzer, Quantachrome Instruments, Boynton Beach, FL). Catalyst (20–100 mg) was degassed by heating to 150 °C (2.5 °C/min heating rate) with He flowing for 30 min and cooled to 50 °C in 60 min. The sample absorbed CO₂ (or NH₃) gas with 10% concentration at 50 °C for 60 min, and was subsequently heated to 700 °C at a heating rate of 5 °C/min with He flowing to determine its basicity or acidity. A blank run for catalyst without absorbing CO₂ (or NH₃) was carried out as background. Three different volumes (0.5, 1, 1.5 mL) of a standard CO₂ (or NH₃) gas (10% CO₂ or NH₃ and 90% He) were used to calibrate basicity or acidity.

2.4. One-step production of biodiesel

Crude *Jatropha* oil or blended soybean oil (about 4.4 g) with different AV (0.7–22.1 mg KOH/g) were reacted in a 50 mL micro high-pressure autoclave (YZPR-50, Yanzheng Shanghai Experimental Instrument Co., Ltd.) for biodiesel production under the given conditions: reaction temperature (120–200 °C, heating time to the desired temperatures is 15–30 min), reaction time (2–6 h, including heating time but excluding cooling time after poweroff), methanol/oil molar ratio (10/1–50/1) and catalyst (1–9 wt%) with magnetic stirring (750 rpm) and initial pressure [3 MPa N₂, reaction pressure of 3.3–5.5 MPa higher than its corresponding saturated methanol vapor pressure, e.g., 4 MPa at 200 °C (Lemmon et al., 2002)] to avoid methanol vaporizing to the dead volume of reactor (about 9.5 mL). All the experiments were repeated twice to improve its accuracy, and the listed biodiesel yields were average of the individual two runs with standard deviation (σ) of 0.1–3.0%.

After biodiesel production, biodiesel, excess methanol, glycerol and catalyst were centrifuged (3–30 K, Sigma Laborzentrifugen GmbH, Osterode am Harz, Germany) for separation at 18,000 rpm (30,427 relative centrifugal force) for 1 min. The used catalyst was washed with pure methanol and dried for next cycles. Crude biodiesel at middle layer (mixed glycerol and methanol) were at upper layer due to high methanol/oil molar ratio) was removed to a 10 mL tube and dried at 105 °C overnight to evaporate methanol. After filtered (pore size 0.22 μ m), biodiesel was analyzed by Gas Chromatography (GC; GC-2014, Shimadzu, Kyoto) with a capillary column of Rtx-Wax (30 m \times \varnothing 0.25 mm \times 0.25 μ m). Analytical conditions were set at column temperature 220 °C, injector temperature 260 °C, detector temperature 280 °C, carrier gas (He) with flow rate of 1 mL/min and the split ratio 40/1. Heptadecanoic acid methyl ester (HAME, C_{17:0}) was used as internal standard to determined biodiesel yield (biodiesel weight measured by GC peaks \times 100%/crude biodiesel weight determined by balance, wt%) based on the weights and GC peak areas of crude biodiesel and HAME. Each peak was calibrated previously (Xue et al., 2014; Zhang et al., 2015) with relative response factors of (1.01, 1.02, 1.08, 1.04, 1.02 and 0.93) for palmitate (C_{16:0}), linolenate (C_{16:1}), stearate (C_{18:0}), oleate (C_{18:1}), linoleate (C_{18:2}) and linolenate (C_{18:3}) methyl esters, respectively.

3. Results and discussion

Catalyst was characterized and used for biodiesel production. Fig. 1 shows TPD results for HT-Ca catalyst. XRD results and the

sizes of different crystal phases in the activated hydrotalcite catalyst (HT-Ca) were summarized in Table 1. Elemental compositions of catalysts by ICP are listed in Table 2. BET surface areas and pore volumes of catalysts are given in Table 3. Single-factor optimized results for *Jatropha* biodiesel production are presented in Table 4. Comparison experiments with HT-Ca vs. HT, Ca(OH)₂ and CaCO₃ catalysts for biodiesel production are shown in Table 5. Detailed results are presented and discussed below.

3.1. Catalyst characterization

3.1.1. XRD and ICP-AES

XRD pattern shows that HT-Ca solid catalyst had well-crystallized structures of (Mg₄Al₂)(OH)₁₂CO₃(H₂O)₃, Mg₂Al(OH)₇, AlO(OH), Mg₄Al₂(OH)₁₄·3H₂O and CaCO₃ as compared with the cards from Joint Committee on Powder Diffraction Standards (JCPDS: 74–0748, 16–0818). The crystalline size was calculated by Scherer equation (Patterson, 1939): $D_c = K\lambda/(\beta \cos \theta)$ (D_c is the average particle size; K , the Scherer constant, is 0.89; λ , the X-ray wavelength of CuK α radiation, is 0.1541 nm; β , full-width at half-maximum; θ , the diffraction angle of the XRD reflection selected). The crystalline sizes of Mg₄Al₂(OH)₁₄·3H₂O, AlO(OH), CaCO₃, Mg₂Al(OH)₇ and (Mg₄Al₂)(OH)₁₂CO₃(H₂O)₃ were about 21.4, 11.7, 44.8, 22.9 and 11.7 nm, respectively (Table 1). CaCO₃ was formed because carbonate anions in the HT layers were replaced by hydroxyls when HT particles were activated with saturated Ca(OH)₂ solution (Fang et al., 2011) which was confirmed according to the formation of Mg₂Al(OH)₇, AlO(OH) and Mg₄Al₂(OH)₁₄·3H₂O. The active composites of HT-Ca enhanced for biodiesel production may be Mg₄Al₂(OH)₁₄·3H₂O and Mg₂Al(OH)₇ (Watanabe and Tatsumi, 1998; Fang et al., 2011), and AlO(OH) (Takagaki et al., 2014). Water-soluble Ca in HT-Ca was measured as 2.1 ppm (30 mg sample dissolved in 50 mL deionized water) by ICP, indicating few Ca(OH)₂ existed in the catalyst because Ca(OH)₂ has a high solubility (1600 ppm) (vs. 6.5 ppm for CaCO₃) at cold water (Lide, 2010). Elemental composition results (Table 2) show that after activation, Mg/Al molar ratio increased from 1.32 for HT to 2.32 for HT-Ca because Al(OH)₃ formed in the step of HT synthesis was further leached into water in aqueous Ca(OH)₂ solution. At the same time, HT-Ca contains 5.1% Ca possibly caused by the formation of CaCO₃. After 1 cycle for biodiesel production, for HT-Ca₁, Ca decreased to 3.5% (from 5.1% for HT-Ca) but Mg/Al molar ratio jumped to 3.24 (from 2.32 for HT-Ca) because of the leaching of CaCO₃ and Al(OH)₃, respectively. If HT was calcined at 300–500 °C, after activation, catalysts (HT300-Ca, HT400-Ca and HT500-Ca) only contain 1.5–2.1% Ca as

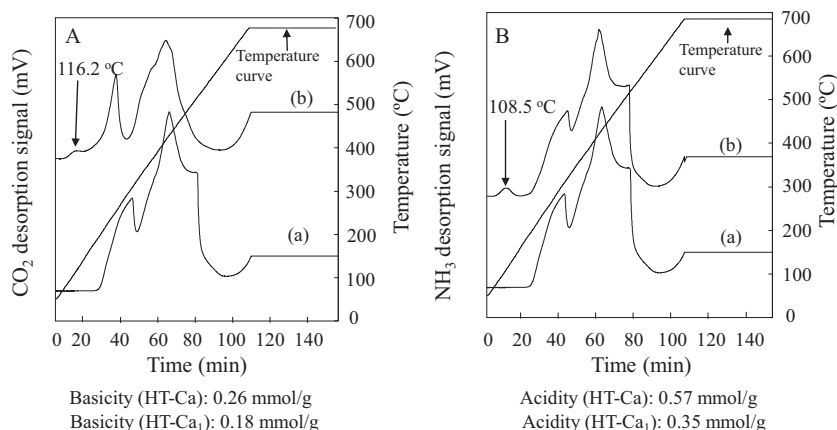


Fig. 1. Temperature programmed desorption (TPD) analyses of activated hydrotalcite catalyst (HT-Ca): (A) CO₂-TPD and (B) NH₃-TPD (a: blank run without CO₂/NH₃ absorption as background).

Table 1XRD diffraction angles (2θ) of different crystal phases from activated hydrotalcite catalyst (HT-Ca) and their sizes calculated by Scherer equation (Patterson, 1939).

Crystal phase	Full-width at half-maximum (β) ^a	2θ (°) ^b		Average particle size (nm)		
Mg ₄ Al ₂ (OH) ₁₄ ·3H ₂ O	0.37° (64.5)	11.6	60.7			21.4
AlO(OH)	0.68° (118.6)	14.4	28.2			11.7
CaCO ₃	0.18° (31.4)	26.2	27.2	38.4	45.9	44.8
Mg ₂ Al(OH) ₇	0.36° (62.8)	34.8	23.4	39.4	62.1	22.9
(Mg ₄ Al ₂)(OH) ₁₂ CO ₃ (H ₂ O) ₃	0.73° (127.3)	46.9				11.7

^a The data in brackets are radian (multiplied by 3.14/180, $\times 10^{-4}$).^b Bold data are used for the calculation of crystalline size.**Table 2**

Elemental compositions of catalysts analyzed by ICP after dissolved by 37% hydrochloric acid.

Catalyst ^a	Mg (wt%)	Al (wt%)	Ca (wt%)	Mg/Al (molar ratio)
HT-Ca	13.89	6.84	5.07	2.32
HT-Ca ₁	13.09	4.63	3.51	3.24
HT	10.70	9.23	–	1.32
HT300-Ca	14.97	5.57	1.46	2.95
HT400-Ca	16.06	5.98	1.65	3.04
HT500-Ca	17.29	11.23	2.10	1.71
HT300-Ca ₁	11.60	4.70	0.28	2.82
HT400-Ca ₁	11.29	4.23	0.81	2.13
HT500-Ca ₁	13.61	8.88	1.70	1.73

^a 300, 400 and 500 are calcination temperatures before activation with aqueous Ca(OH)₂ solution, subscript 1 means catalyst after the first cycle.

compared to 5.1% Ca for HT-Ca without calcination. The low Ca content was from the decarbonating of HT [occurred at 250–450 °C (Watanabe and Tatsumi, 1998)] that would not form low water-soluble CaCO₃ in activated process to contribute Ca. However, low Mg/Al molar ratio (1.71) was found for HT500-Ca. This is because when HT calcined at 500 °C, most aluminum compounds [e.g., HT and Al(OH)₃] turned into Al₂O₃ (Watanabe and Tatsumi, 1998) that may have a lower solubility in aqueous Ca(OH)₂ solution.

3.1.2. TPD, SEM-EDX and BET

CO₂-TPD and NH₃-TPD profiles of HT-Ca show a weak peak for basicity and acidity at 116.2 and 108.5 °C, respectively with a strong background at higher temperatures (>200 °C) (Fig. 1) owing to the thermal decomposition of HT-Ca (Reyero et al., 2013). Basicity and acidity of HT-Ca were only 0.26 and 0.57 mmol/g, and reduced further to 0.18 and 0.35 mmol/g for HT-Ca₁, after 1 cycle for biodiesel production.

SEM images illustrate that HT-Ca nanoparticles had sheet structures but slightly agglomerated after 1 cycle. EDX spectra demonstrate that the catalysts (HT-Ca and HT-Ca₁) were composed of Mg 17.2 and 14.6%, Al 20.6 and 16.7%, C 19.0 and 28.1%, O 42.8 and 39.7%, Ca 0.5 and 0.9% (H undetectable by EDX) with low Ca content (<1% vs. 5.1% for HT-Ca by ICP) and low Mg/Al molar ratio (55.1/58.6 and 26.7/27.1 vs. 2.32/1 for HT-Ca by ICP). The low Ca content on the surface proved that CaCO₃ was formed and

Table 3

BET surface areas and pore volumes of different catalysts (HT-Ca, HT, HT300-Ca, HT400-Ca and HT500-Ca).

Catalyst ^a	BET surface area (m ² /g)	Pore volume (cm ³ /g)
HT-Ca	24.69	0.16
HT	3.70	0.04
HT300-Ca	35.82	0.24
HT400-Ca	47.11	0.34
HT500-Ca	53.90	0.33

^a 300, 400 and 500 are calcination temperatures before activation with aqueous Ca(OH)₂ solution.

precipitated in the inter-layers of HT by replacing carbonate anions with hydroxyls. While most of AlO(OH) precipitated on the surface and resulted in low Mg/Al molar ratio.

After activation, both surface area and pore volume jumped dramatically from 3.7 to 24.7 m²/g, 0.04 to 0.16 cm³/g for HT and HT-Ca, respectively (Table 3). The sharp increases were caused by ion exchanges in the activated process. If calcination, after activation, surface area and pore volume of catalyst rose much higher to 35.8, 47.1 and 53.9 m²/g, as well as to 0.24, 0.34 and 0.33 cm³/g for HT300-Ca, HT400-Ca and HT500-Ca because numerous micropores produced during pyrolysis step at 300–500 °C (Zhang et al., 2014; Watanabe and Tatsumi, 1998).

3.2. Biodiesel production

Single-factor optimization of *Jatropha* biodiesel production with activated hydrotalcite HT-Ca was conducted (*Jatropha* oil AV: 6.3 mg KOH/g, magnetic stirring: 750 rpm, and initial N₂ pressure: 3 MPa) and results are summarized in Table 4.

3.2.1. Reaction temperature

Since HT-Ca presented weak acidic and basic, high reaction temperature from 120 to 200 °C (Dawodu et al., 2014; Shu et al., 2010) was applied for biodiesel production under conditions of 5 wt% catalyst, 4 h reaction time and methanol/oil molar ratio of

Table 4

Jatropha biodiesel yield changed with variables: (a) reaction temperature, (b) methanol/oil molar ratio, (c) catalyst dosage, and (d) reaction time. (4.4 g *Jatropha* oil with AV of 6.3 mg KOH/g, magnetic stirring of 750 rpm, and initial N₂ pressure of 3 MPa in a 50 mL autoclave. Bold data are values for a variable changes under given conditions or biodiesel yield under best conditions.)

Temperature (°C)	Methanol/oil molar ratio	Catalyst (wt%)	Time (h)	Biodiesel yield (wt%)
(a)				
120	20	5	4	10.3 ± 0.4
140	20	5	4	30.5 ± 1.3
160	20	5	4	63.8 ± 0.6
180	20	5	4	69.4 ± 0.6
200	20	5	4	67.7 ± 0.5
(b)				
160	10	5	4	42.3 ± 0.8
160	20	5	4	63.8 ± 0.6
160	30	5	4	82.7 ± 0.8
160	40	5	4	91.2 ± 1.2
160	50	5	4	93.4 ± 0.4
(c)				
160	40	1	4	86.4 ± 1.5
160	40	3	4	86.5 ± 0.5
160	40	5	4	91.2 ± 1.2
160	40	7	4	86.7 ± 2.0
160	40	9	4	81.3 ± 0.3
(d)				
160	40	5	2	67.3 ± 3.0
160	40	5	3	81.6 ± 1.5
160	40	5	4	91.2 ± 1.2
160	40	5	5	91.6 ± 0.6
160	40	5	6	92.4 ± 0.8

Table 5
Biodiesel yield in the presence of different catalysts with same Ca content.

Catalyst	Catalyst weight (g) ^a	Biodiesel yield (%)
Ca(OH) ₂	0.041	84.0 ± 0.3
CaCO ₃	0.056	3.9 ± 0.1
HT	0.220	53.9 ± 0.2
HT-Ca	0.22 (5 wt%)	93.4 ± 0.8

^a All catalysts have the same Ca content as HT-Ca except HT. (Reaction conditions: 160 °C, 4.5 MPa, 4 h and 30/1 methanol/oil molar ratio with 6.3 mg KOH/g *Jatropha* oil AV, 750 rpm magnetic stirring and 3 MPa initial N₂ pressure.)

20/1. When temperature grew from 120 to 160 °C, biodiesel yield jumped sharply from 10.3% to 63.8%. After that, biodiesel yield gradually grew to the maximum of 69.4% at 180 °C, and slightly decreased to 67.7% at 200 °C. Since only a slight biodiesel yield increased at >160 °C, reaction temperature of 160 °C is selected as the best value in the following experiments.

3.2.2. Methanol/oil molar ratio

Much wider range of methanol/oil molar ratio [(10/1–50/1 vs. 12/1–16/1 (Xue et al., 2014))] was selected to optimize biodiesel yield since the autoclave has a relative large dead volume (9.5 mL vs. 50 mL reactor volume and 4.4 g crude *Jatropha* oil). Other reaction conditions are selected as: 160 °C for 4 h with 5 wt% catalyst. Biodiesel yield grew sharply from 42.3% to 82.7% and gradually to the maximum of 93.4%, as methanol/oil molar ratio rose from 10/1 to 30/1 and 50/1. So, high molar ratio of methanol/oil is required for achieving ideal biodiesel yield because of high reaction temperature 160 °C and large dead volume. The best methanol/oil molar ratio is selected as 40/1 with 91.2% biodiesel yield.

3.2.3. Catalyst dosage

Catalyst amount of 1–9 wt% [vs. 3–7 wt% (Xue et al., 2014)] was selected to produce biodiesel at 160 °C for 4 h with 40/1 methanol/oil molar ratio. Biodiesel yield rose slightly to the maximum of 91.2% from 86.4% to 86.5% as catalyst increased from 1 to 3 and 5 wt%. When catalyst amount increased further to 9 wt%, biodiesel yield declined gradually to 81.3% because of poor mixture between solid and liquid (Xue et al., 2014). Therefore, 5 wt% catalyst is selected for the next experiments.

3.2.4. Reaction time

Reaction time of 2–6 h was used for biodiesel production under given conditions (160 °C, 5 wt% catalyst, 40/1 methanol/oil molar ratio). Biodiesel yield increased rapidly to 91.2% at 4 h, and slightly rose further to 92.4% at 6 h due to reaction equilibrium. Therefore, the best conditions with 91.2 ± 1.2% biodiesel yield are chosen as 160 °C, 4 h, 5 wt% catalyst and 40/1 methanol/oil molar ratio.

Since high methanol/oil molar ratio of 40/1 was required due to large dead volume for the above best conditions that will cause high cost for excess use of methanol. Therefore, experiments with more oil sample (or more methanol) but low molar ratio were conducted. Double oil weight (*Jatropha* oil 8.8 g) with 5 wt% catalyst at 160 °C was tested at methanol/oil molar ratio of 20/1, 25/1 and 30/1, biodiesel yields of 81.4 ± 1.8%, 84.5 ± 0.9% and 93.4 ± 0.8% were achieved, respectively. Methanol/oil molar ratio of 30/1 is selected as the best value.

In conclusion, the best conditions with biodiesel yield of 93.4 ± 0.8% for the production of *Jatropha* biodiesel with HT-Ca nanoparticles are reaction temperature of 160 °C, methanol/oil molar ratio of 30/1, 5 wt% catalyst and reaction time of 4 h. These conditions were used in the following experiments with different AV, catalysts calcined at 300–500 °C, different Ca catalysts and catalyst cycles.

3.2.5. Biodiesel production at different acid values

Jatropha and blended soybean oils with different AV were selected as raw materials to evaluate HT-Ca resistance to FFAs in the production of biodiesel under the above best conditions.

Jatropha biodiesel gradually declined from 93.4 ± 0.8% to 81.0 ± 0.3% and 82.5 ± 0.6% from AV of 6.3 to 12.8 and 17.2 mg KOH/g. For soybean oil, biodiesel yield presented a peak of 92.9% at AV of 12.1 mg KOH/g with yields of (85.9 ± 0.1%, 86.0 ± 0.1%, 92.9 ± 0.2%, 89.2 ± 0.4% and 88.4 ± 0.1%) at AV of (0.7, 6.8, 12.1, 18.1 and 22.1 mg KOH/g). There is a best AV (6.3 and 12.1 for *Jatropha* and soybean oils) for biodiesel yield because high AV may cause saponification of FFAs by basic sites, while low AV means less biodiesel from esterification by acidic sites but incomplete transesterification by weak basic sites of this catalyst.

3.2.6. Biodiesel production with catalysts at different calcination temperatures

Jatropha oil with AV of 6.3 mg KOH/g was selected as raw oil to test the activity of HT-Ca, HT300-Ca, HT400-Ca and HT500-Ca under the above best conditions. *Jatropha* biodiesel yield is 93.4 ± 0.8%, 82.1 ± 0.6%, 83.7 ± 1.6% and 91.7 ± 1.9% under the calcination temperature of 0 (without calcination), 300, 400 and 500 °C, respectively. These results show that calcination step before activation did not increase catalyst activity. HT500-Ca had higher activity than HT300-Ca and HT400-Ca mainly because of the formation of the strong basic oxides (e.g., MgO and Al₂O₃) in calcination process (Watanabe and Tatsumi, 1998) and higher specific surface area (Table 3) caused by the release of CO₂ and H₂O at high temperature.

3.2.7. Biodiesel production with different Ca catalysts

Since Ca(OH)₂, CaCO₃ and HT are starting activation materials or activated by-product, they were chosen as catalysts to produce *Jatropha* biodiesel to verify the effectiveness of activation of HT. Catalysts with the same Ca content as HT-Ca (5 wt% or same weight for HT) were applied for the comparison experiments under the above best conditions (Table 5). Biodiesel yields of only 84.0%, 3.9% and 53.9% were achieved for Ca(OH)₂, CaCO₃ and HT catalysts, much lower than 93.4% for HT-Ca. The higher activity of activated HT-Ca was possibly from Mg₄Al₂(OH)₁₄·3H₂O and Mg₂Al(OH)₇ as base, and AlO(OH) as acid.

3.2.8. Catalyst cycles

In order to test the stability of HT-Ca catalyst, it was recycled for *Jatropha* biodiesel production under the above best conditions after reaction, centrifugal separation, washed with methanol for three times, dried at 105 °C overnight and ground in a mortar. Five cycles were conducted with HT-Ca, catalyst amount used declined gradually with dosage of (0.44 ± 0.0007, 0.46 ± 0.0035, 0.33 ± 0.0064, 0.23 ± 0.0071 and 0.12 ± 0.0000 g or 5.0, 5.2, 3.8, 2.6 and 1.4 wt%) for 1–5 cycles (with biodiesel yields of 93.4 ± 0.8%, 86.9 ± 0.9%, 88.1 ± 0.8%, 86.7 ± 1.1% and 69.6 ± 0.6%) due to the weight loss during collecting and washing process except the second cycled catalyst with weight growth (5.2 wt%) caused by soap formation. Biodiesel yield dropped gradually from 93.4% to 86.7% at the fourth and further declined to 69.6% at the fifth cycles. The reasons for the yield decline are: (i) catalyst loss (5 wt% at the beginning vs. 1.4 wt% at the fifth cycle); (ii) catalyst agglomeration caused by slight saponification; (iii) loss of catalytic active sites due to the dissolution of Mg, Al and Ca; and (iv) glycerol remained on the surface of the catalyst.

4. Conclusions

Activated Mg–Al hydrotalcite-calcium nanoparticles were synthesized and showed high activity to produce biodiesel from crude

oils with high acid value without pretreatment. The catalyst presented both acidic and basic to catalyze esterification and transesterification due to the formation of $Mg_4Al_2(OH)_{14}\cdot 3H_2O$, $Mg_2Al(OH)_7$ and $AlO(OH)$ nanoparticles. It can resist free fatty acids to achieve 93.4% *Jatropha* biodiesel yield at AV of 6.3 mg KOH/g and recycle 4 times with biodiesel yield >86%. Soybean biodiesel yield reached 92.9% even from oil with high AV of 12.1 mg KOH/g.

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