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Magnesia modified with strontium as a solid base catalyst for transesterification of palm olein

Boonyawan Yoosuk[a], Pawnprapa Krasae[a], Buppa Puttasawat[a], Parncheewa Udomsap[a], Nawin Viriya-empikul[b], Kajornsak Faungnawakij[b,*]

[a] National Metal and Materials Technology Center (MTEC), 114 Thailand Science Park, Phahonyothin Road, Klong 1, Klong Luang, Pathumthani 12120, Thailand
[b] National Nanotechnology Center (NANOTEC), 111 Thailand Science Park, Phahonyothin Road, Klong 1, Klong Luang, Pathumthani 12120, Thailand

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ABSTRACT

This paper reports the possibility of using magnesia modified with strontium as a solid catalyst for biodiesel production via transesterification reaction. A synergetic effect between active Sr species and MgO support was clearly evidenced by the comparative study. Fine particles of the Sr–Mg catalysts prepared by the impregnation synthesis exhibited excellent activity as compared to bulk dense SrO or less-active MgO alone. The high activity of the Sr–Mg catalyst could result from the new strong basic-sites generated from the solid phase reaction and the high dispersion of the active species, as suggested from characterization data. The study shows that the amount of Sr in the catalyst and the calcination temperature are crucial factors affecting the catalyst performance; the optimal preparation condition was that with a Sr loading amount of 5.0 mmol/g and a calcination temperature of 600 °C. The methyl ester (ME) content of 97.3 wt.% was achieved over the developed catalyst within 30 min under the optimal transesterification conditions of methanol:oil molar ratio of 9:1, catalyst amount of 5 wt.% and temperature of 60 °C. The present study provides new insight into controlling the catalyst activity of magnesia modified with strontium by tailoring the preparation conditions.

1. Introduction

Given the depletion of petroleum, many countries are looking to other sources of fuel for their energy needs. In this regard, biodiesel is an interesting alternative to diesel fuel that has several benefits: it is a renewable source that provides complete combustion and emits less pollution-causing gas than do other fuel [1]. Therefore, biodiesel has attracted worldwide attention and is already being used commercially in a number of countries. Transesterification processes with homogeneous base catalysts such as NaOH, KOH, and $NaOCH_3$ are currently used extensively in biodiesel production. However, these homogeneous catalysis systems have many drawbacks [2]. Removing these catalysts in order to purify the biodiesel fuel and glycerol as a by-product is difficult and requires a large amount of water. Consequently, a considerable amount of waste water is inevitably produced [1,3]. To overcome these problems, using a transesterification process with environmentally friendly solid catalysts is a promising route.

Heterogeneous catalysis is an economically and ecologically important field in catalysis research because heterogeneous catalysts have many advantages: non-corrosive and environmentally friendly, they present fewer disposal problems than do homogeneous catalysts. They are also much easier to separate from liquid products and can be designed to give higher activity, better selectivity, and longer catalyst lifetimes [4]. Recently, the French Institute of Petroleum (IFP) commercialized the first heterogeneously catalyzed biodiesel production process known as the Esterfip-HTM process; this process operates in a continuous mode, includes two successive fixed bed reactors, and uses a spinel mixed oxide of Zn and Al as a solid base catalyst [5,6]. Although the activity of this catalyst is relatively low, necessitating the use of high reaction temperatures (200 °C), it is reported to show very stable operation with no metal leaching (i.e., no formation of metal glycerate or carboxylate salts). The purity of the methyl esters produced is claimed to exceed 99 wt.%, with yields close to 100 wt.% of theoretical.

Many types of heterogeneous solid base catalysts, such as alkaline-earth metal oxides and hydroxides, have been studied for the transesterification of vegetable oils [4,7], various alkali metal compounds supported on alumina [8–10], zeolite [11], hydrotalcites [12], anion exchange resins [13], and polymer-supported guanidines [14]. The order of activity among alkaline-earth oxide catalysts is BaO > SrO > CaO > MgO [12,15]. The active ingredients in

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* Corresponding author. Tel.: +66 2564 7100x6638; fax: +66 2564 6981.
E-mail address: kajornsak@nanotec.or.th (K. Faungnawakij).

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most supported alkali catalysts are easily corroded by methanol and have short catalyst lifetimes. However, in most of the experiments using heterogeneous catalysts, the transesterification reaction proceeds at a relatively slow rate compared to those conducted with homogeneous catalysts. The slow reaction rates are due to diffusion problems accruing from the behavior of heterogeneous media such as a three-phase system (oil/methanol/catalyst) [9]. Thus, the development of a solid basic catalyst to carry the transesterification of oils efficiently under mild reaction conditions in short reaction times remains an intriguing challenge.

It has been reported that SrO can catalyze many chemical reactions, such as oxidative coupling of methane, selective oxidation of propane, nitroaldol reactions and mixed tishchenko reactions, and transesterification [16,17]. It has basic-sites stronger than $H_- = 26.5$ [18], and is insoluble in methanol, vegetable oils, and fatty acid methyl ester. Liu et al. observed that a biodiesel yield of >95 wt.% can be achieved within 30 min by using SrO as solid base catalyst [16]. This study showed that SrO has a long catalyst lifetime and can maintain sustained activity even after being repeatedly used, in this case, for 10 cycles.

A solid of great technical significance, magnesia (magnesium oxide, MgO) is widely used as a refractory material. Its catalytic interest lies in its essentially basic surface character, which makes it an effective catalyst and catalyst support [19]. Magnesium oxide exhibits strong basicity by virtue of the presence of surface O^{2-} ions that capture protons readily. It also exhibits weak Lewis basicity, which is ascribed to Mg^{2+} ions [20]. MgO is mainly obtained by thermally treating magnesium hydroxide or carbonate, and, more recently, by the sol–gel method. Textural and acid–base properties depend, to a great extent, on synthesis conditions: the pH, gelifying agent, sequence of the addition of reagents, calcination temperature, etc. [21]. Several studies have focused on modifying the cation of MgO acid–base characteristics in the presence of other species, such as other oxides, metallic ions, and noble metals, establishing this approach as a very effective way of tailoring the activity towards many organic processes [13,22]. These studies emphasize the advantages that can accrue from the co-existence of two different basic oxide components in the catalyst for transesterification.

To the best of our knowledge, no study on the catalytic performance of magnesia modified with strontium in the transesterification of vegetable oils has been published. In the present study, we have examined the activity of strontium-modified magnesia catalysts for the transesterification of palm olein. The catalysts were prepared via a conventional impregnation method, and their physicochemical properties studied using various characterization techniques. The study also investigated the impact of catalyst preparation conditions and the transesterification reaction conditions on the methyl ester content.

2. Experimental

2.1. Chemicals and catalyst preparation

Magnesia modified with strontium catalysts was prepared by using incipient wetness impregnation of aqueous solutions of the corresponding metal salt precursors on magnesia. Magnesium carbonate ($MgCO_3$) purchased from Himedia was used as the starting material for magnesia support. $MgCO_3$ was calcined at 800 °C for 3 h in order to change it from a carbonate form to an oxide one. The salt precursor applied was an analytical-grade nitrate salt of strontium ($Sr(NO_3)_2$) purchased from Aldrich. Magnesia was dispersed in deionized water under vigorous stirring at 70 °C. An aqueous solution of $Sr(NO_3)_2$ of the desired amount was then added dropwise into slurry. After the solution had been mixed well for about 2 h, the resulting slurry was heated at 120 °C overnight to remove residual moisture. Before being used as a catalyst in the transesterification process, the dried solid was calcined at the desired temperature for 4 h to elevate catalytic activity. The strontium oxide (SrO) catalyst was prepared by calcining the $Sr(NO_3)_2$ at 600 °C for 4 h. Thereafter, the magnesia modified with the strontium catalyst was designated as MS-X, with X representing the mmol of Sr/g of the magnesia.

2.2. Catalyst characterization

The N_2 adsorption and desorption isotherms were measured on a Micromeritics ASAP 2020 instrument. The pore-size distributions of the samples were determined from the isotherms by the Barrett–Joyner–Hallenda (BJH) method [23]. Fresh samples were dried before the adsorption measurement was made. The X-ray diffraction (XRD) patterns were obtained on a JEOL JDX-3530 theta-2theta X-Ray diffractometer with Cu Kα emission with 0.02° per step. The diffractograms were analyzed using the standard JCPDS files. The morphological study was carried out with an S-3400 Hitachi scanning electron microscope. The thermal decomposition of the sample was evaluated by thermo-gravimetric analysis (TGA) carried out on a Mettler Toledo thermogravimeter (TG/DTG) at a ramping rate of 10 °C/min under dry air flow.

The basicity of catalyst was studied by temperature programmed desorption (TPD) using CO_2 as a probe molecule. Prior to CO_2 adsorption, catalysts (0.3 g) were pretreated under a nitrogen stream at 120 °C for 30 min (10 °C/min and 20 mL/min). Then, the temperature was decreased to room temperature, and a flow of pure CO_2 (20 mL/min) was subsequently introduced into the reactor for 150 min. The system was flushed with N_2 for 60 min. The TPD of CO_2 was carried out under a helium flow at a flow rate of 20 mL/min. The temperature was ramped from 40 to 960 °C and held at this temperature for 60 min with a temperature ramp of 10 °C/min. The CO_2 desorption was monitored by an online gas chromatograph provided with a thermal conductivity detector (TCD).

2.3. Transesterification reaction

The palm olein oil was purchased from Morakot Industries PCL, Thailand. The composition of fatty acid in palm olein oil is given in Table 1. The methanol used in this work was of analytical reagent grade and was purchased from Fluka. The transesterification was carried out in batch reactor. A 500 mL round-bottom flask equipped with a reflux condenser was used. The magnetic stirring rate of 500 rpm was adjusted and the reaction temperature was controlled by a hotplate with a temperature sensor (Heidolph). Palm olein oil in an amount of 50 mL was warmed at 60 °C before being added to the mixture of methanol and catalyst that had already been heated

Table 1
Fatty acid compositions of palm olein oil used in the present study.

Fatty acid	Composition (wt.%)
Lauric acid (C12:0)	0.4
Myristic acid (C14:0)	0.8
Palmitic acid (C16:0)	37.4
Stearic acid (C18:0)	3.6
Arachidic acid (C20:0)	0.3
Saturated	42.5
Palmitoleic acid (C16:1)	0.2
Oleic acid (C18:1)	45.8
Linoleic acid (C18:2)	11.1
Linolenic acid (C18:3)	0.3
Eicosenoic acid (C20:1)	0.1
Unsaturated	57.5
Total fatty acid	100.0

to 60 °C. The mixture's temperature was kept at 60 °C by an oil bath. The methanol:oil molar ratio and catalyst-loading amount varied between 3:1 and 21:1 and 0–7 wt.% of starting oil weight, respectively. After the desired reaction time, the product of the reaction was separated from the catalyst by centrifugation, and the excess amount of methanol was evaporated before the ME content was analyzed.

The yield and compositions of the methyl ester products were determined by a gas chromatograph (GC-2010, Shimadzu) equipped with a capillary column, DB-WAX (30 m × 0.15 mm) and a flame ionization detector. The column temperature was programmed from 180 to 230 °C with the heating rate of 5 °C/min. Methylheptadecanoate was used as an internal standard for quantification. The percentage of methyl esters was calculated based on the standard method EN 14103. Both Duplicate and triplicate experiments were performed, but only the average of the duplicated tests is reported here. The errors for % ME content values were typically within plus/minus 1.0 wt.%. In addition, the palm olein oil used as a raw material for biodiesel production has a low acid value of 1.10 mg KOH/g oil, whereas the final biodiesel products have a low acid value of ca. 0.20 (±0.05) mg KOH/g oil. The acid values meet the ASTM D664 standard (≤0.50 mg KOH/g oil).

3. Results and discussion

3.1. Strontium oxide, magnesia, and strontium-modified magnesia

The ME contents obtained from the transesterification reaction over SrO, MgO, and MS-2.0 are shown in Table 2. Over SrO with BET surface area of 0.5 m^2/g, the ME content reached 85.5 wt.% at 30 min. On the other hand, MgO has very low catalytic activity: no methyl ester was observed within 30 min. After the impregnation of Sr onto MgO (2.0 mmol of Sr/1 g of MgO), the ME content of 84.3 wt.% was obtained over the supported catalyst. As compared to pure SrO, MS-2.0 showed the comparable activity despite having a lower Sr content. However, when 0.5 wt.% of pure SrO, which contains the same mole of Sr as MS-2.0, was applied to the reaction, a very low ME content was observed. These results indicate that Sr species has a significant synergetic effect on the MgO catalyst for the transesterification activity.

The surface area of catalysts measured before the transesterification reaction is shown in Table 2. The pure SrO had very low surface area as compared to the others. When Sr was loaded onto MgO, the surface area of the MS-2.0 is approximately 14.2 times higher than that of pure SrO while the MgO catalyst has a surface area equal to 4.7 times that of MS-2.0. These results suggested that impregnating MgO with Sr species influences the surface area of MgO and helps to disperse the Sr species.

The surface morphology of the SrO, MS-2.0 and MgO was examined using SEM technique, as shown in Fig. 1. The pure SrO (Fig. 1A) comprised large particles, exposing smooth planes or regularly facetted steps. Impregnating MgO with Sr generated a high density of irregular, pitted small particles, and a highly textured and rough surface was revealed (Fig. 1B). This finding explains the increase in surface area of the MS-2.0 catalyst as compared to pure SrO. This morphology result is also consistent with the surface area results showing that Sr component is highly dispersed after being impregnated onto MgO.

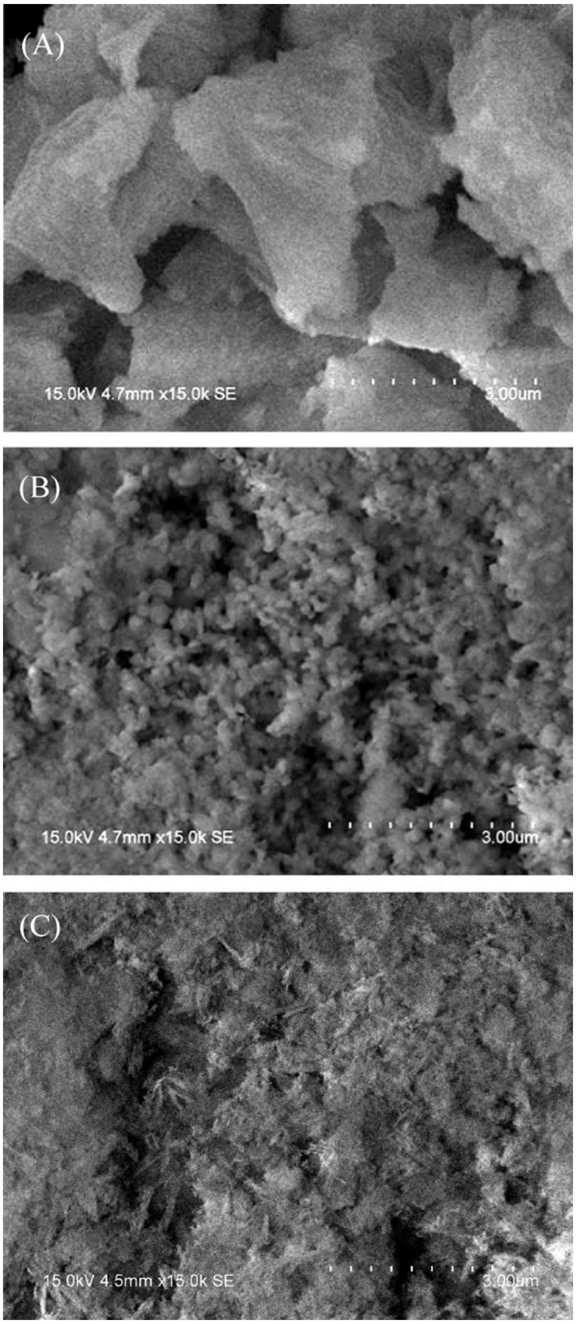

Fig. 1. SEM images of (A) pure SrO, (B) MS-2.0 and (C) MgO.

Table 2
Properties and activities of SrO, MgO, and MS-2.0 catalysts.

Catalysts	Loading amount in the reaction (wt.%)	ME content[c] (wt.%)	Surface area (m^2/g)
SrO[a]	3.0	85.5	0.5
SrO[a]	0.5	5.4	0.5
MS-2.0	3.0	84.3	7.6
MgO[b]	3.0	0.0	35.3

[a] Calcined $Sr(NO_3)_2$ at 600 °C for 4 h.

[b] Calcined $MgCO_3$ at 800 °C for 3 h.

[c] Reaction conditions: methanol:oil molar ratio, 9:1; temperature, 60 °C; reaction time, 30 min.

The weight loss and DTG curves of the MS-2.0 and $Sr(NO_3)_2$ catalyst before the calcination are shown in Fig. 2. The samples were dried at 120 °C overnight prior to analysis. As shown in Fig. 2(A), no obvious peak in the temperature range below 300 °C corresponded even loosely to the elimination of the surface in either of the profiles, suggesting that the surface physisorbed water was removed during the dryness. $Sr(NO_3)_2$ showed a one-step decomposition starting from 540 to 684 °C with two DTG peaks (Fig. 2(B)) that have the maxima at 638 and 666 °C. The non-calcined MS-2.0

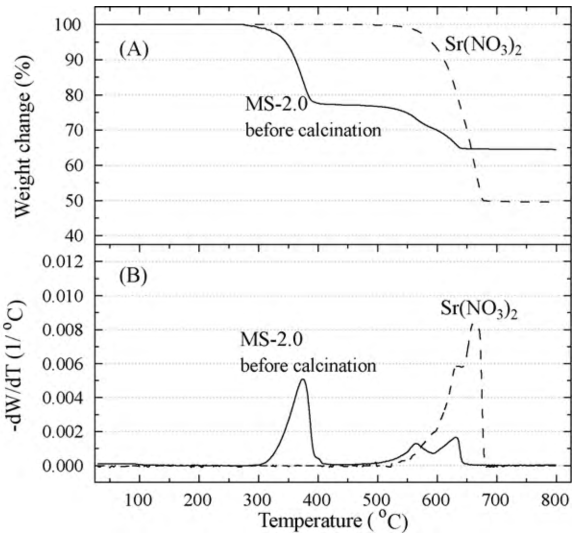

Fig. 2. (A) Weight loss and (B) DTG curves of $Sr(NO_3)_2$ and MS-2.0 before calcination.

catalyst showed two major weight-loss peaks; one in the temperature range of 300–385 °C and the other in the temperature range of 460–660 °C. The total weight loss was 35%. The first weight-loss step with a maximum DTG peak at 368 °C accounted for 24% of the material weight. In comparison with the authentic sample, this peak was attributed to the weight loss of $Mg(OH)_2$ to form MgO. The second weight-loss step exhibited a similar decomposition pattern as pure $Sr(NO_3)_2$, but with a low intense DTG peak. The DTG peaks have maxima at 570 and 635 °C. It can be seen that these two DTG peaks shifted to a lower temperature. This result suggests that the incorporation of Sr onto Mg decreases the temperature required for $Sr(NO_3)_2$ to decompose to SrO. This weight-loss step might be ascribed mainly to the combination of the decomposition of the $Sr(NO_3)_2$ and the solid state interaction between the guest compound with the support. The literature also shows that the textural properties of the MgO solid surfaces are affected by the presence of a second precursor and the preparation procedure, and this is in good agreement with the findings of other authors [24,25].

The diffraction pattern of the samples was probed by powder XRD as shown in Fig. 3. Magnesia catalyst exhibits sharp diffraction peaks at 36.8°, 42.8° and 62.3° which is characteristic of well crystallized MgO (periclase). No diffraction peak of carbonate/hydroxide species was detected. For the bulk strontium oxide catalyst, the crystalline phases that can be assigned to SrO (30.0°, 34.8° 50.2°, 59.4° and 62.4°) and $Sr(OH)_2$ (27.2°, 28.7°, 36.6°, 38.6°, 43.6° and 46.8°) were observed. Thus, XRD results confirmed that the oxide form of Mg and Sr were obtained after thermal decomposition of parent materials. However, the appearance of hydroxide species was detected for only bulk strontium catalyst. This indicated that the hydration of SrO occurs more rapidly than that of MgO. In the case of strontium-modified magnesia, the crystalline phases present in the MS-2 catalyst correspond to MgO (periclase), SrO, and $Sr(OH)_2$.

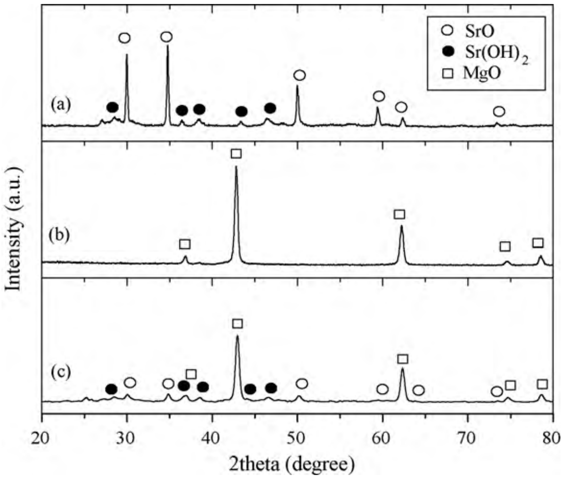

Fig. 3. XRD patterns of (a) SrO prepared from $Sr(NO_3)_2$ calcined at 600 °C, (b) MgO prepared from $MgCO_3$ calcined at 800 °C, and (c) MS-2.0.

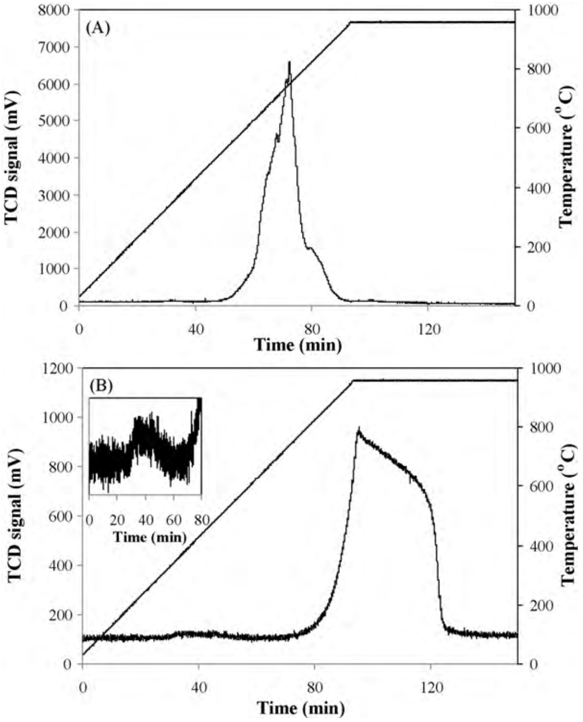

Fig. 4. CO_2-TPD profiles of (A) SrO and (B) MS-2.0.

Fig. 4 shows the rate of CO_2 desorption (CO_2-TPD), normalized to the sample loading, as a function of the run time and temperature for SrO and MS-2.0 catalysts. The SrO showed the desorption peak at the high temperature of 746 °C with very high intensity. This peak might be attributed to the presence of strong basic sites, corresponding to isolated O^{2-} anions. After the impregnation of Sr onto MgO, MS-2.0 catalyst showed a broad desorption curve at temperatures higher than 950 °C which is higher than that of pure SrO. This high desorption temperature could be due to the presence of much stronger basic sites (superbasic), probably corresponding to isolated O^{2-} but located in a particular position of the surface. It should be noted that MS-2.0 also exhibited a very small intensity desorption peak at the temperature of 344 °C. This low temperature peak was predominant for MgO in MS-2.0, as compared to the authentic sample. It can be attributed to basic sites of medium strength related to oxygen in Mg^{2+}–O^{2-} pairs.

As the TPD results, the new stronger basic-site (the desorption temperature more than 950 °C) was observed only for MS-2.0 and the basic-site belong to SrO was present at the temperature of 746 °C. Accordingly, it is very likely that the new basic site was attributed to the new active species generated during the catalyst synthesis. These active species might be the results of the solid phase reaction of ion exchange perhaps occurred between Mg^{2+} and Sr^{2+} at 600 °C, and Mg^{2+} and Sr^{2+} were originated from magnesia and SrO from the decomposition of $Sr(NO_3)_2$, respectively. This phenomenon was also observed when hydroxyapatite loaded with strontium was calcined at 600 °C as reported by Chen et al. [26]. This new species resulted by the solid phase reaction was claimed as the main reasons for the catalytic activity towards the transesterification reaction. Sree et al. [22] also reported the strong interaction between MgO and ZrO_2 in the Mg/Zr catalyst leading to the stronger basic site as compared to that of MgO and ZrO_2.

Taking into account all the results obtained from the transesterification reaction and characterization, it could be suggested that the main active site in the catalyst probably comes from two species. The first one could be the SrO derived from the thermal decomposition of $Sr(NO_3)_2$ after calcination. The small SrO particles formed on MgO prepared by a suitable impregnation followed by calcination could give better basicity than bulk dense SrO, unsupported catalyst. Another one could be the new species generated from the solid-state reaction between the guest compound and the support in the calcination process, when the Sr species is loaded on the support. This is expected for the catalyst to achieve high catalytic activity. It has also been suggested that a synergetic effect between the active metal oxides and supports or within the metal oxide particles is responsible for many heterogeneously acid–base-catalyzed reactions [27,28]. The increase in ME content of MS-2.0 as compared to pure SrO (0.5 wt.%) as shown in Table 2 could result from the new stronger basic-site presented in MS-2.0 and the high dispersion of the active species.

The basic sites in the alkali earth metal oxides can be supposed to be due to the presence of the M^{2+}–O^{2-} ion pair in different coordination environments (M stands for metal component). Various oxygen anions of low coordination number on the MO are considered to be responsible for the basicity [29]. The strength of the basic site is likely related to the electro-negativity of the conjugated metal cation. When the high level of electro-negativity intensified the electron attractive force for the conjugated metal cation, the basic characteristics of the oxygen anion deteriorated. Concerning transesterification with methanol, catalytic reactions take place on the surface of the solid base catalysts. In the first step, surface O^{2-} extracts proton (H^+) from methanol to form surface methoxide anion (CH_3O^-), which is strongly basic and has high catalytic activity in the transesterification reaction [4]. The methoxide anion attacks carbonyl carbon in a molecule of the triglyceride, which leads to the intermediate formation of alkoxycarbonyl on the catalyst surface. Then, the intermediate picks up H^+ from the surface of the catalyst or it reacts with methanol to generate methoxide anions [1]. In the final step, the alkoxycarbonyl intermediate divides into two molecules: fatty acid methyl ester (FAME) and anion of diglyceride.

3.2. *Effect of catalyst preparation conditions*

As discussed, magnesia modified with strontium is an attractive catalyst for biodiesel production under the employed reaction conditions. Therefore, the effects of catalyst preparation conditions on the activity of magnesia modified with strontium were evaluated through the transesterification of palm olein with the reaction conditions (methanol:oil molar ratio, 9:1; temperature, 60 °C; and reaction time, 30 min).

Fig. 5 graphically illustrates the evolution of the ME content for a series of the strontium content in Sr–Mg catalysts, activated at 600 °C for 4 h. It can be seen that the ME content was greatly dependent on the amount of loaded strontium. The catalysts with the low loading amount of Sr, 1.0 mmol/g, exhibited very low ME formation. When the amount of loaded Sr increased from 1.0 to 1.5 mmol/g, the ME content was significantly enhanced and came up to the maximum value of 97.7 wt.% at the Sr loading amount of 5.0 mmol/g. However, a further increase in the amount of loaded Sr beyond 5.0 mmol/g decreased the ME content.

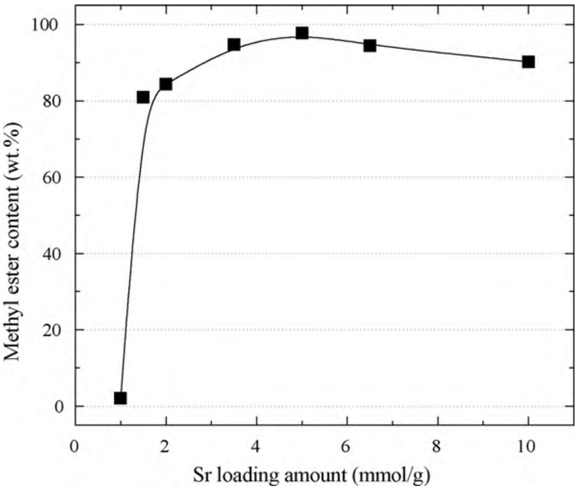

Fig. 5. Dependence of methyl ester content on Sr loading amount for Sr/Mg catalysts. Reaction conditions: methanol:oil molar ratio, 9:1; temperature, 60 °C; catalyst amount, 3 wt.%; and reaction time, 30 min.

The increase in ME content in the range of the Sr loading amount of 1.0–5.0 mmol/g was likely because more active catalyst particles were formed as more Sr species were loaded onto the MgO. Adding more amount of Sr does not increase the catalytic activity, presumably due to the poor dispersion of SrO. Yang and Xie [30] reported a decrease in the conversion of triglyceride when ZnO was loaded with $Sr(NO_3)_2$ higher than 2.5 mmol/g. They also showed a good correlation between the basicities and activities of the catalyst. In addition, the optimal Sr loading amount for the Sr/Mg catalyst was 5.0 mmol/g, higher than that for the ZnO loaded with the $Sr(NO_3)_2$ catalyst (2.5 mmol/g). The higher dispersion of the active species and the more active phase generated probably accounts for this difference. The reduction of surface area was found after impregnation of Sr on MgO. The catalyst with Sr loading amount of 1.0 mmol/g has the surface area of 11.3 m^2/g. Surface area of catalyst decreased with the increasing of Sr loading amount. At the loading amount of 1.5–5.0 mmol/g, surface area was in the range of 8.0–4.2 m^2/g. Beyond 5.0 mmol/g, the surface area was dramatically decreased to below 1.0 m^2/g, confirming the poor dispersion of the loaded particles. Given the present results, the catalyst with the loading amount of Sr of 5.0 mmol/g is the most suitable formulation for transesterification.

The calcination temperature has been reported to be an important parameter affecting the surface basicity of the catalyst, i.e., the site strength, as well as site concentration and accessibility. As discussed in regard to the thermal decomposition results (Fig. 2), the temperature during heat treatment affects the formation of SrO and MgO in the catalysts. To determine the influence of the calcination temperature on catalytic activity, the samples were activated at different temperatures (500–1200 °C) and then used for palm olein transesterification with methanol at 60 °C.

The effect of the calcination temperature on the activity of MS-2.0 is shown in Fig. 6. The results indicate that the catalytic activity of MS-2.0 is strongly dependent on the calcination temperature. No methyl ester was observed when non-calcined MS-2.0 was used (data not shown). This suggests that the basicity of the nitrate form of strontium is not high enough to catalyze the transesterification reaction. A very low ME content was also observed after calcinations at 500 °C. This result corresponds with the thermal decomposition profile, which shows that the temperature of 500 °C was too low to effectively decompose $Sr(NO_3)_2$ to active SrO. When the temperature was increased to 550 °C, an ME content of 89.3% was obtained. Calcination of the catalyst at 600 °C results in the most active MS-2.0 catalyst, giving an ME content of

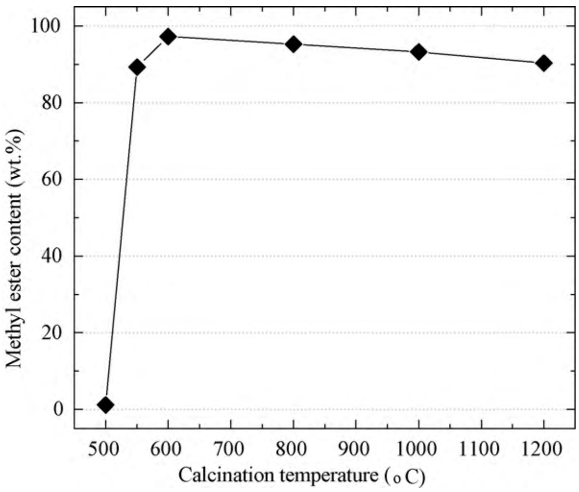

Fig. 6. Dependence of methyl ester content on calcination temperature over MS-2.0 catalysts. Reaction conditions: methanol:oil molar ratio, 9:1; temperature, 60 °C; catalyst amount, 5 wt.%; and reaction time, 30 min.

96.5%. The results suggest that a high-temperature pretreatment is necessary for the catalyst to achieve an activity sufficiently high for the transesterification. However, the ME content decreased when the calcination temperature was further increased. This should be due to the sintering effect, which causes an agglomeration of SrO and MgO clusters.

The basicity of the nitrate form of strontium is not high enough for this reaction; therefore, the activity variation of the catalysts calcined at different temperatures should be attributed to the different extents to which the $Sr(NO_3)_2$ decomposed. The results indicate that the calcination temperature has to be high enough to break down the ordered structure, remove the counterbalancing anions, and induce phase transitions within the oxide lattice. Yet, the calcination temperature must also be low enough to avoid agglomeration the SrO and MgO clusters.

3.3. *Effect of transesterification reaction conditions*

One of the important parameters that affect the conversion triglyceride is the molar ratio of methanol to oil. The stoichiometry of this transesterification reaction requires 3 mol methanol per 1 mol triglyceride in order to yield 3 mol biodiesel and 1 mol glycerol. But given that transesterification is a reversible reaction, the use of a large amount of alcohol should benefit the conversion of TGs from the standpoint of thermodynamics. However, high alcohol:lipid molar ratio has been reported to slow down the reaction owing to a diminution in catalyst concentration by a large excess of alcohol [31].

Fig. 7 illustrates the evolution of the ME content for a series of methanol:oil molar ratios as a function of time in transesterification. As a result, the ME content increased rapidly in the reaction time of 30 min for all reaction tests. The performance of the MS-2.0 catalyst strongly depended on the methanol:oil ratio. It can be seen that the ratio of 3:1 which is the stoichiometric ratio shows the lowest ME content throughout the reaction course (50.1 wt.% at 30 min). The increase in the methanol:oil ratios typically enhanced the ME content, especially at the beginning of the reaction course. The greatest yield of biodiesel was obtained at 97.3% for the methanol:oil ratio of 9:1 at 30 min, though the initial reaction rate for the methanol:oil ratios of 15:1 and 21:1 was faster. It was considered that the high methanol content (beyond the ratio of 9:1) favorably induced the reversible reaction of transesterification of high biodiesel yield. Since the transesterification is a base-catalyzed reaction of a reversible nature, it is likely that the reverse transesterification occurs between the methyl ester product and glycerol, forming monoglycerides and diglycerides that behave molecularly like a co-solvent, and homogenize the products [32]. This might cause ME content to decrease at a high methanol:oil ratio. Additionally, increasing the ratio above 9:1 does not only lower the ME content, but also makes the ester recovery process complicated and raises its cost. The difficulty of separating of methyl esters and glycerol was observed at a high methanol:oil ratio. This might be because methanol has a polar hydroxyl group that can act as an emulsifier causing emulsification. Other researchers have also observed this phenomenon [8,16]. Note that no soap formation was observed in any of the experiments. Based on the present evaluation, the amount of methanol at the optimum ratio of 9:1 is sufficient to disperse oil and catalyst phases, and to facilitate the transesterification.

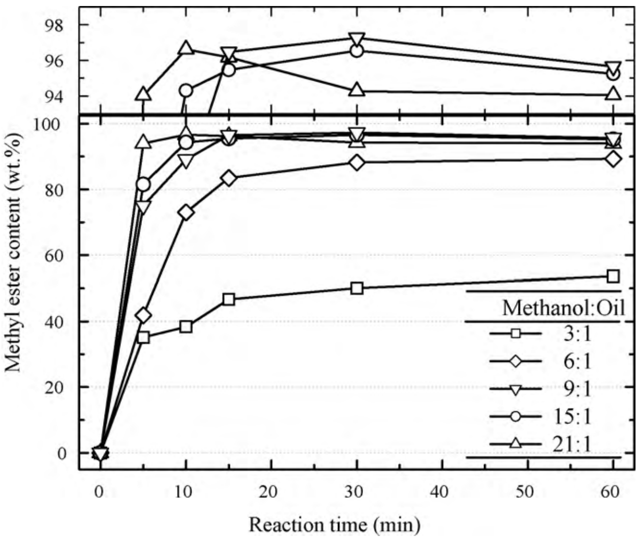

Fig. 7. Reaction time dependence of methyl ester content over MS-2.0 catalysts with various methanol:oil molar ratios. The expanded scale for the ME content above 93 wt.% is shown in the top part of the figure. Reaction conditions: catalyst amount, 5 wt.%; temperature, 60 °C.

The transesterification process involves three stepwise reversible reactions. First, triglycerides (TG) present in oil are converted to diglycerides (DG). The second step is the conversion of diglycerides to monoglycerides (MG), which are finally converted to glycerol. Each step produces a molecule of ME. The reaction proceeds via the nucleophilic attack of the methoxide species, which is thought to be responsible for the active sites [4], on a carbon atom of the carbonyl groups of glycerides, resulting in the formation of ME. Since the reactions are reversible, it is likely that the final extent to which the oil is converted mainly depends on the methanol:oil ratio. The amount of methanol used in excess with respect to the stoichiometric relation helps to shift the reaction towards the ME formation. The presence of a sufficient amount of methanol during the transesterification reaction is essential to break the glycerin–fatty acid linkages [33], and the usage of excess methanol is one of the better options for improving the slow reaction rate of the transesterification reactions catalyzed by heterogeneous catalysts. However, it is worth noting that the use of a large excess of methanol may not be the only or most efficient way to speed up the reaction rate. A recent study using triacetin reported that catalyst surface hydrophobicity may be a key factor governing product selectivity in TG transesterification [34].

In the heterogeneous catalysis system, the reaction mixture consists of three phases (oil/methanol/catalyst). The active methoxide species is formed upon adsorption of methanol on the catalyst sur-

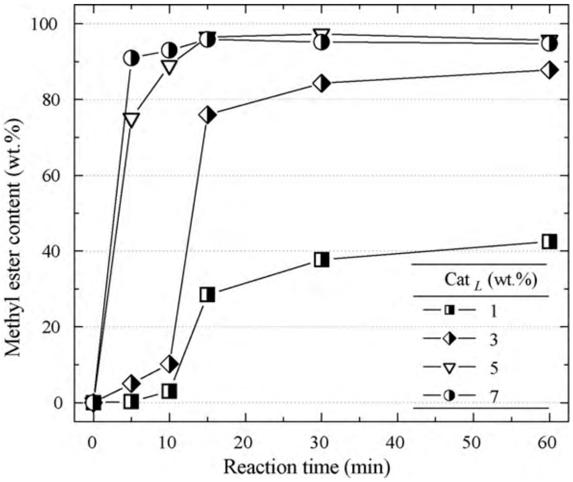

Fig. 8. Reaction time dependence of methyl ester content over MS-2.0 catalysts with various catalyst-loading amounts (Cat_L). Reaction conditions: methanol:oil molar ratio, 9:1; temperature, 60 °C.

face, and the transesterification reaction becomes mass-transfer controlled [9]. Knowledge of how heterogeneous catalysts kinetically affect transesterification is very limited at the moment. However, it has been reported that, in the presence of solid base catalysts, the reaction involves the active participation of methoxide species, and then, the efficiency of the catalyst should be related to the rate of formation of methoxide anion [35]. Dossin et al. [36] studied the kinetics of the transesterification of ethyl acetate with methanol by using MgO as a catalyst. They found that methanol adsorption was the rate-determining step. This result is compatible with our results since as the methanol:oil ratio increases the driving-force for methanol adsorption increases as well, thus favoring the transesterification reaction. This is in contrast with the use of NaOH (methanol soluble) as a catalyst, for which the reaction mixture is a two-phase oil:methanol system wherein the amount of methanol has little effect on the formation of the methoxide species. In this case, the initial transesterification rate is determined by the concentration of NaOH in the methanol phase, that is, the NaOH:methanol ratio [37].

It has been reported that the amount of catalysts has a strong effect on ME content in the case of homogeneous catalysts, as the initial reaction rate is determined by the concentration of homogeneous catalyst in the methanol [37]. Therefore, the effect of the catalyst-loading amount was investigated for the MS-2.0 catalyst at a methanol:oil molar ratio of 9:1. Fig. 8 graphically illustrates the evolution of the ME content for a series of catalyst-loading amounts (0–7 wt.%) as a function of time in transesterification. The results indicate that the ME content is strongly dependent on the amount of catalyst applied. In the absence of the catalyst, no ME formed in the reaction mixture. A catalyst amount of 1 wt.% also showed a low ME content of approximately 42.5 wt.% at 60 min. The higher amount of catalyst loading was, the greater ME content obtained. When the catalyst amount increased from 1 to 3 wt.%, the ME content increased to 87.8 wt.% at 60 min. Applying a catalyst amount of 5 wt.% yielded the highest ME content of 97.3 wt.% at a short reaction time of 30 min. The further increment of the catalyst amount up to 7 wt.% could increase the biodiesel production rate only in the reaction time range below 30 min. Above this point, the ME content was not yielded to overcome that obtained with the catalyst loading of 5 wt.%. This effect has also been reported by other researchers [30,38]; it is probably due to a mixing problem involving reactants and the solid catalyst provoking in the reaction media at the high biodiesel yield condition.

These results suggest that the increased amount of methyl esters produced is due to an increase in the number of basic sites in the reaction system. It has been reported from comparative studies of various solid catalysts in soybean oil transesterification that the activity of catalyst in the transesterification reaction is closely related to the number of basic sites [39]. However, from the results, the effect of the catalyst amount on ME content was slight when the catalyst amount was above 3 wt.%. It is probably more important to intensify mass transfer than to increase the amount of the catalyst. It is noteworthy that the magnesia modified with the strontium catalyst showed high activity even at low concentrations of the catalyst.

Reusability is one of the most important features for a heterogeneous catalyst that is to be used commercially. Thus, the reusability of strontium-modified magnesia was examined by carrying out subsequent reaction cycles. After each cycle, reaction mixtures were carefully withdrawn, the catalyst sediment recovered, and a new reaction cycle started with fresh reactants. The collected catalysts were used directly without re-calcination. During the whole process, care was taken to minimize the exposure time of the catalysts to the atmosphere, thus limiting possible site contamination by CO_2.

Fig. 9 shows the reusability of the strontium-modified magnesia catalyst in the transesterification of palm olein. It was revealed that the collected catalyst was not as active as the fresh one. The catalyst can be repeatedly used three times with the ME content over 85 wt.% maintained. However, in the fourth and fifth runs, the ME content decreased. For basic oxides, metal ion leaching into solution is always a primary concern directly affecting catalyst deactivation characteristics. The elemental analysis of the mixture after reaction using atomic absorption spectroscopy (AAS) showed that there is the amount of metal fraction that remained in the reaction mixture, suggesting that the catalyst has lost some active species during the transesterification process. The amounts of Mg and Sr in the biodiesel product were 24 and 842 ppm, respectively. These results suggested that leaching is one of the factors caused the reduction of activity.

An attempt was made to regenerate the used catalyst by impregnation with an $Sr(NO_3)_2$ aqueous solution as described in the experimental section. The regenerated catalyst showed the high activity. The ME content of 95.7 wt.% was obtained under the same reaction conditions as fresh catalysts. Hence, the result was implying that the catalyst could be regenerated by this method.

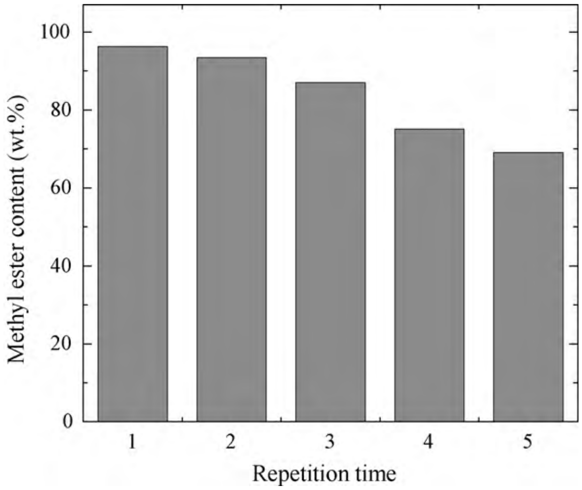

Fig. 9. Reusability of MS-5.0 catalyst in the transesterification of palm olein. Reaction conditions: methanol:oil molar ratio, 6:1; catalyst amount, 10 wt.%; time 15 min; temperature, 60 °C.

Table 3
Comparison of the transesterification activity of the MS-2.0 catalyst with reported solid base catalyst.

Conditions and ME content	SrO	SrO/ZnO	Hydroxyapatite loaded with Sr	Hydrotalcite loaded with Sr	MS-2.0	Nano CaO	CaO/ZnO
Sr on catalyst (wt.%)	100	14.5	8.3	1.5	14.5	–	–
Catalyst loading (wt.%)	2.0	5.0	5.6	1.5	5.0	1.1	10.0
Methanol:oil molar ratio	9:1	9:1	9:1	20:1	9:1	9:1	30:1
Reaction temperature (°C)	65	65	70	60	60	Room temperature	60
Reaction time (h)	0.5	5.0	5.0	3.0	0.5	24.0	3.0
ME content (wt.%)	93	92	85	56	97	85	94
Reference	[16]	[30]	[26]	[38]	Present study	[40]	[41]

3.4. *Activity comparison of the strontium-based catalysts*

The transesterification activity of MS-2.0 was compared to other reported Sr-based catalysts [16,26,30,38] and Ca-based ones [40,41]. The results, summarized in Table 3, show that all the catalysts are very impressive in terms of catalytic activity; this is with the exception of hydrotalcite loaded with Sr, which shows low activity of 56 wt.% ME content. This might be because the latter catalyst has a smaller amount of catalyst loading and a smaller amount of Sr. It could be seen that strontium is an efficient catalyst and promoter of supported catalyst for the transesterification reaction. Chen et al. [26] reported that when strontium was loaded on hydroxyapatite, the new phase $Ca_xSr_{1-x}O$ was generated by the solid phase reaction of the ion exchange between hydroxyapatite and loaded strontium under 600 °C. This new phase was thought to be responsible for the high catalytic activity. However, a new phase was not reported for any other catalyst. An insufficient or excess amount of loaded Sr is responsible for the low activity of most of the listed catalysts. The amount of loaded Sr that causes the highest catalytic activity strongly depends on the type of support.

For the other cited catalysts (non strontium based), the data show that they are reported under reflux conditions and took a longer reaction time to achieve complete conversion of oil. Reddy et al. [40] reported room temperature transesterification of soybean oil using nanocrystalline CaO. The catalyst showed high conversion of oil at the reaction time of 24 h. In comparison to the above listed catalysts (Table 3), the activity of the present catalyst appears very impressive in term of its shorter reaction time and smaller methanol to oil molar ratio.

4. Conclusions

The study of solid base catalysts is a promising route for developing a better heterogeneous catalytic system capable of carrying the transesterification of oils proficiently under mild reaction conditions in short reaction time. The present results show that the active mixed oxide of Sr and Mg for the transesterification reaction can be successfully prepared by an impregnation method followed by calcination. The fine particles of the catalyst exhibited excellent activity as compared to bulk SrO or non-active MgO, indicating the synergetic effect over the Sr–Mg oxide nano-composite.

The catalyst with a Sr loading amount of 5.0 mmol/g of MgO exhibited the best catalytic activity, suggesting the largest amounts of active sites. When more Sr is added, the active phase may not be well dispersed, and results in reduced activity. The calcination temperature was found to largely influence the catalytic activity of the resultant catalysts. The temperature must be high enough to break down the ordered structure, yet low enough to avoid agglomeration. A temperature of 600 °C was found to be suitable, as it resulted in complete decomposition and yielded the most active MS-2.0 catalyst. The reaction conditions (methanol:oil molar ratio, catalyst amount, and reaction time) have a significant effect on the activity of catalyst. The most suitable conditions for the transesterification of palm olein oil over the magnesia modified with strontium catalyst were found to be a methanol:oil molar ratio of 9:1, a catalyst amount of 5 wt.%, and a reaction time of 30 min conditions that yielded an ME content of 97.3 wt.%.

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