Biguanide-functionalized mesoporous SBA-15 silica as an efficient solid catalyst for interesterification of vegetable oils

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A B S T R A C T

The biguanide-functionalized SBA-15 materials were fabricated by grafting of organic biguanide onto the SBA-15 silica through covalent attachments, and then this organic–inorganic hybrid material was employed as solid catalysts for the interesterification of triacylglycerols for the modification of vegetable oils. The prepared catalyst was characterized by FTIR, XRD, SEM, TEM, nitrogen adsorption–desorption and elemental analysis. The biguanide base was successfully tethered onto the SBA-15 silica with no damage to the ordered mesoporous structure of the silica after the organo-functionalization. The solid catalyst had stronger base strength and could catalyze the interesterification of triacylglycerols. The fatty acid compositions and triacylglycerol profiles of the interesterified products were noticeably varied following the interesterification. The reaction parameters, namely substrate ratio, reaction temperature, catalyst loading and reaction time, were investigated for the interesterification of soybean oil with methyl decanoate. The catalyst could be reused for at least four cycles without significant loss of activity.

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1. Introduction

The physicochemical and functional properties of fats and oils are determined by their compositions of fatty acid (FA) residues and the positions on the glycerol backbone of triacylglycerols (TAGs). Most native vegetable oils have limited applications in food products when used in their original forms. Hydrogenation and interesterification are the main methods employed for the modification of edible lipids to meet the specifications for certain food applications (Fauzi, Rashid, & Omar, 2013; Xu, 2000). Partial hydrogenation can convert liquid oils to semi-solid fats; however in this chemical process *trans* FAs are inevitably produced. The formed *trans* FAs are known to be undesirable from a nutritional standpoint, since they have been shown to increase the risk of coronary artery disease (Dhaka, Gulia, Ahlawat, & Khatkar, 2011). Recently, the interesterification of vegetable oils has received much interest in the edible oil industry as a feasible method to improve their physicochemical characteristics, by rearranging the positional distribution of FAs located in the glycerol backbone of TAG molecules (Costales-Rodríguez, Gibon, Verhé, & De Greyt, 2009; Paula, Nunes, de Castro, & Santos, 2015). More importantly, unlike the hydrogenation, the interesterification process does not produce *trans* FAs and does not affect the degree of saturation

(Ribeiro, Grimaldi, Gioielli, & Gonçalves, 2009). By using the catalytic interesterification, structured lipids can be produced by varying the FA profiles and/or positional distribution in the glycerol backbone so as to provide the desired physical and nutritional properties (Soares et al., 2009).

Industrially, the interesterification reaction has long been used for the modification of fat and oil mixtures. This chemical process is frequently carried out using sodium hydroxide and sodium alkoxide as a catalyst (Meng, Liu, Shan, Jin, & Wang, 2010; Raquel, Véronique, Roland, & Wim, 2009; Rousseau, Marangoni, & Jeffrey, 1998). Although these homogeneous catalysts are relatively inexpensive and readily available, their removal and subsequent product purification steps after the interesterification process are required and a large amount of wastewater is produced. More recently, one of the challenges in the field of catalysis is to replace homogeneous catalysts by heterogeneous ones owing to the advantages of green or sustainable chemistry for catalyst recovery, easier operation and reutilization (Semwal, Arora, Badoni, & Tuli, 2011). To date, numerous studies have been conducted on heterogeneous base catalysts for various organic reactions, including supported alkali or alkaline earth metals, basic zeolites, hydrotalcites, zeolites, and ion-exchange resins (Semwal et al., 2011; Xie & Zhao, 2013, 2014). In particular, the immobilization of organic base on solid supports, such as guanidines immobilized on polymers or encapsulated in zeolite cages, has recently drawn considerable attention as a new generation of heterogeneous base catalyst because of the

superior catalytic activities, excellent stabilities, ease of separation and satisfactory reusability in comparison to the conventional homogeneous catalysts (Schuchardt, Sercheli, & Vargas, 1998; Schuchardt, Vargas, & Gelbard, 1996). However, to our knowledge, little attention has been paid to heterogeneous base catalysts for the interesterification of vegetable oils, despite their promising catalytic efficiency in other organic transformations (Xie & Qi, 2013).

Mesoporous molecular sieves have recently been highlighted in the literature, especially in regard to their applications in heterogeneous catalysis (Lebeau, Galarneau, & Linden, 2013). SBA-15 silica, as one class of these inorganic mesoporous silica materials, has been identified as an important support material of heterogeneous catalysts thanks to its well-ordered structure, and large surface area; in particular, sufficient silanol groups on the pore surfaces can be facilely functionalized with organic compounds (Prasetyanto & Park, 2008). In the past decades, organically functionalized mesoporous materials have generated a great deal of interest. Grafting of organic base groups on the surface of the mesoporous material can be considered as an efficient approach to create the inorganic–organic hybrid solid base catalysts (Bhange, Bhange, Pradhan, & Ramaswamy, 2011; Yue et al., 2008). This heterogeneous hybrid catalyst can be separated easily from the product, resulting in no wastewater originating from the catalyst neutralization step.

Guanidine and biguanide, as strong organic bases, are commonly used as homogeneous base catalysts in organic synthesis (Ishigawa, 2009). These types of guanidine bases can be easily anchored onto the mesoporous silica materials by co-condensation of organic base with the support to afford the hybrid solid catalyst with the preservation of a pore host structure. For example, the 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, a bicyclic guanidine base) covalently grafted onto SBA-15 nanoparticles is a robust heterogeneous catalyst employed for biodiesel production under solvent-free condition (Nguyen, Nohair, Mighri, & Kaliaguine, 2013). Besides this, our previous work has reported a guanidine-immobilized SBA-15 composite catalyst, and it exhibited catalytic activities towards the interesterification of soybean oil and methyl stearate (Xie, Yang, & Zang, 2015). Biguanides are stronger base than amines, amidines and guanidines due to the presence in their structure of two imine groups adjacent to three amino groups (Ishigawa, 2009). As such, the biguanide-functionalized SBA-15 materials are expected to be utilized as stronger solid base catalysts than the guanidine-functionalized ones for the interesterification of vegetable oils.

In recent years, the development of nontoxic and recyclable solid catalysts with improved efficiency has been the subject of immense interest and can also meet green chemistry demands. However, eco-friendly catalysis processes for modifying fats and oils by utilizing solid catalysts have seldom been reported in literature until lately (Xie & Qi, 2013). As a part of our efforts to fabricate solid catalysts for the interesterification of vegetable oils, the biguanide-functionalized SBA-15 materials were prepared in the current research by attachment of a biguanide on SBA-15 silica through a covalent bond linkage. Such hybrid materials can offer a new possibility for developing an environmentally friendly heterogeneous interesterification process since they can combine the superiority of both homogeneous base catalyst and solid catalyst with a single material. Thus, the novelty of the present work is associated with the preparation of a new inorganic–organic hybrid material with mesoporous structure and its successful application in the interesterification reaction for the modification of vegetable oils in a heterogeneous manner. The as-prepared solid hybrid catalyst was characterized in detail by means of Fourier transform infrared (FT-IR) spectra, nitrogen adsorption–desorption,

small-angle X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and elemental analysis techniques. By using the solid base catalyst, the heterogeneous interesterification of soybean oil with methyl decanoate was carried out to optimize the reaction parameters. Under the optimized conditions, the binary blends of palm stearin and soybean oil at different substrate ratios were interesterified for the production of structured lipids. The TAG compositions and FA profiles of the initial blends and the interesterified products were investigated by gas chromatography (GC) and high-performance liquid chromatography (HPLC) techniques. Finally, the recyclability of the hybrid solid catalyst was also tested through consecutive catalytic runs.

2. Material and methods

2.1. Materials

Methyl decanoate ($\geqslant$98%) was obtained from Sinopharm Chemical Reagent Corporation (Sanghai, China). Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, M_W = 5800), (3-chloropropyl)triethoxysilane ($\geqslant$98%), 1,1,3,3-tetramethylguanidine (TMG, $\geqslant$98%), diisopropyl-carbodiimide (DIC, $\geqslant$98%) and tetraethylorthosilicate (TEOS, $\geqslant$98%) were purchased from Sigma–Aldrich. Soybean oil was obtained from a commercial source. According to GC (Shimadzu DC-9A) analysis, the FA profile was shown as follows: 11.2% palmitic acid (P), 4.6% stearic acid (St), 23.2% oleic acid (O), 53.6% linoleic acid (L), 7.2% linolenic acid (Ln) and traces of other FAs. Palm stearin was provided by Wilmar Biotechnology Research and Development Center (Shanghai, China) and its FA composition was as follows: 85.1% palmitic acid, 9.0% oleic acid, 4.4% stearic acid, and 4.7% linoleic acid. Pancreatic lipase (type II from porcine pancreas) powder was acquired from Sigma–Aldrich. All the other materials used were of either analytical or chromatographical grades.

The biguanide base, 1,2-diisopropyl-4,4,5,5-tetramethylbiguanide, was prepared according to the method reported in the literature and was identified by FT-IR, ^{1}H NMR, ^{13}C NMR and melting point determinations (Gelbard & Vieffaure-Joly, 1998).

2.2. Catalyst preparation

Mesoporous SBA-15 silica was prepared according to methodology described previously (Yue et al., 2008). As shown in Fig. 1, for the synthesis of solid hybrid catalyst, the chloropropyl-functionalized SBA-15 silica was firstly prepared and then 1,2-diisopropyl-4,4,5,5-tetramethylbiguanide was immobilized onto the SBA-15 silica through the condensation of the biguanides with chloropropyl groups. Typically, 1 g of SBA-15 silica was added to a solution of 3-chloropropyl-trimethoxysilane (2.4 g) in dry toluene (30 ml), after which the resulting mixture was stirred for 48 h at reflux temperature under nitrogen atmosphere. The chloropropyl-functionalized SBA-15 silica thus obtained was separated by filtration, washed subsequently with toluene and methanol, and extracted for 6 h using a 1/1 methylene chloride/diethyl ether mixture.

In the next step, the chloropropyl-functionalized SBA-15 (1.5 g) was added into a solution of biguanide (2.2 g) and sodium methylate (0.35 g) in dry toluene (30 ml), and the resultant mixture was stirred continuously under nitrogen atmosphere at reflux for 24 h. Finally, the obtained biguanide-functionalized SBA-15 silica was collected by filtration, extracted for 6 h with a 1/1 methylene chloride/diethyl ether mixture, followed by drying at 60 °C for 12 h under vacuum prior to use.
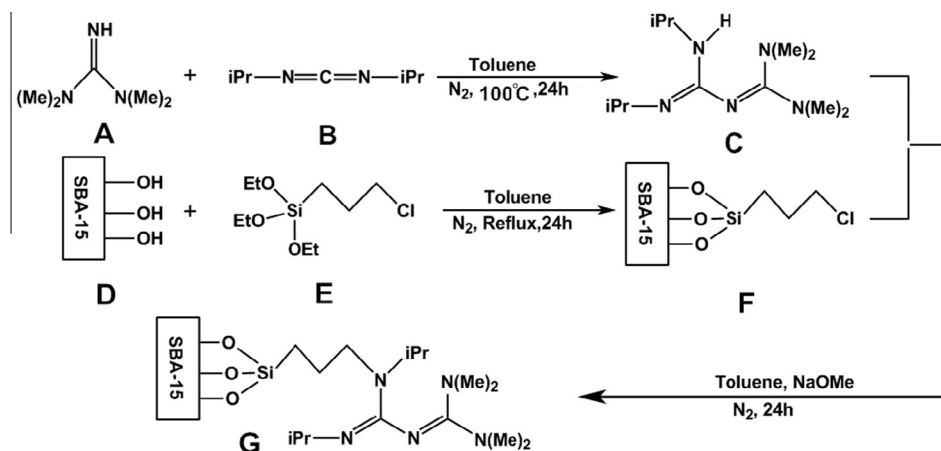
Fig. 1. Synthesis of SBA-15-pr-biguanide solid base catalyst.

2.3. Catalyst characterization

Small-angle X-ray powder diffraction (XRD) patterns were acquired on a Rigaku D/MAX-3B powder X-ray diffractometer with the Cu Kα radiation source of wavelength 0.154 nm. Fourier transform infrared spectra (FTIR) were recorded with a Shimadzu IR-Prestige-21 spectrometer using KBr pressed powder discs. Scanning electron microscope (SEM) measurements were conducted with a field-emission microscope (JEOL, JSM-6390LV) using an accelerating voltage of 15 kV. Transmission electronic microscopy (TEM) images were recorded on a JSM-6390LV transmission electronic microscope.

The nitrogen porosimetry measurements were carried out on a Quantachrome NOVA 1000e instrument at liquid nitrogen temperature (−196 °C). The specific surface area was calculated following the Brunauer–Emmett–Teller (BET) method. The pore volume and pore size distribution were obtained by using the Barrett–Joyner–Halenda (BJH) method applied to the adsorption branch of the nitrogen adsorption–desorption isotherm. Elemental analyses for C, H, and N were performed by Carlo-Erba 1106 elemental analyzer. The extent of biguanides loaded on the SBA-15 silica was measured by the elemental analysis.

2.4. Interesterification procedures

The catalytic activity of the biguanide-functionalized SBA-15 silica was tested by two different interesterification reactions. The batch interesterification of soybean oil with methyl decanoate was performed in a 50 ml round-bottom flask. In a typical assay, 8.7 g (0.01 mol) of soybean oil and 7.5 g (0.04 mol) of methyl decanoate were mixed under vigorous stirring. Prior to the interesterification, the substrate mixtures were dried under reduced pressure with a rotary evaporator at a temperature of 60 °C. By adding 1.6 g of the solid hybrid catalyst, the heterogeneous reactions were carried out in solvent-free media under reduced pressure at 90 °C. After the required reaction duration, the reactor was cooled to room temperature. The solid catalyst was then recovered from the reaction mixture by simple filtration, and reused in the next cycle with fresh reaction mixture several times.

By using the catalyst, the interesterification of soybean oil and palm stearin blend was also carried out at laboratory scale. Initially, soybean oil and palm stearin were blended in different 70:30, 60:40, 40:60, 30:70 proportions (w/w) and then portions (100 g) of the blends were heated under vacuum at 60 °C to homogenize the reaction mixture and to remove moisture. When the reaction mixture reached a temperature of 90 °C, a certain amount of the solid catalyst was added into the batch reactor, and the formulated blends were stirred vigorously. The heterogeneous interesterification of soybean oil and palm stearin blend was conducted under reduced pressure at 90 °C with magnetic stirring (~750 rpm) for a timeframe of 4 h. After completion of the reaction, the interesterified product was filtered and then used for subsequent analysis. All assays were performed in duplicate, and the means were employed for the evaluation of the results.

2.5. Analytical methods

The FA compositions were determined by gas chromatography (GC) according to AOAC Official Method Ce 2-66 (AOCS, 2009). After the FA residues were completely converted into their corresponding fatty acid methyl esters (FAMEs), the methylated FA residues were assessed using an Agilent 6890 N gas chromatograph fitted with a flame-ionization detector and a fused-silica capillary column (60 m × 0.25 mm) coated with 0.25 μm of BPX-70 (SGE, Australia). The carrier gas was nitrogen at a flow rate of 1.2 ml/min with a split ratio of 1:20. The FAME composition was identified by comparing the relative retention time of the peaks with those of the respective FAME standards. The FAME content was obtained by area normalization and expressed as mass percentage, according to the AOCS Official Method Ce 2-66 (AOCS, 2009).

For the interesterification of soybean oil with methyl decanoate, the quantification of decanoyl incorporation into the TAGs of soybean oil was carried out after separation of the TAG fraction by thin-layer chromatography (TLC) on silica gel 60G plates. The interesterified blends were spotted on TLC silica gel plates, and then developed with acetic acid/ethyl ether/petroleum ether (1:10:90, v/v/v). The developed TLC plates were air-dried and sprayed with a solution of 0.2% 2,7-dichlorofluorescein in 95% ethanol. Bands corresponding to TAGs, which were identified using triolein as the standard, were scrapped from the silica plates, extracted using n-hexane and finally analyzed to determine the FA profiles.

To determine the sn-2 positional FA composition, the obtained TAGs were hydrolyzed selectively to 2-monoacylglycerols using pancreatic lipase according to the method described in the literature (AOCS, 2009), and then the 2-monoacylglycerol formed was methylated and analyzed by GC techniques as described previously.

For the interesterification of soybean oil with palm stearin, the TAG compositions of the products were analyzed using high-performance liquid chromatography (HPLC) (AOCS, 2009). The samples of reaction mixtures, corresponding to different reaction

conditions, were dissolved in chloroform (10 mg/ml), and aliquots of the dissolved samples (20 µl) were injected into the HPLC system equipped with an evaporative light-scattering detector (ELSD). The chromatographic separation of TAG species was achieved with a commercially packed Genesis C18 column (150 mm × 4.6 mm). The mobile phase was a mixture of acetonitrile and dichloromethane at an elution rate of 1.2 ml/min. The gradient started with 30% dichloromethane and 70% acetonitrile and held for 25 min, and was then programmed to increase dichloromethane content from 30% to 70% over 45 min. Identification of TAG species was achieved by comparison of retention times with those of the standards and also according to the literature (Silva et al., 2009; Soares et al., 2009). Quantification of the peaks was made by internal normalization of chromatographic peak area, and the results were expressed in terms of the relative area percentage.

The iodine value (IV) was calculated from the FA composition, according to the procedure described in the AOCS Official Method Cd 1c-85 (AOCS, 2009). Slip melting point (SMP) was determined according to the AOCS Official Method Cc 3-25 (AOCS, 2009) using the open capillary tube method.

2.6. Recycling of the solid catalyst

Recyclability of the catalyst was evaluated for the interesterification of soybean oil with methyl decanoate. After completion of the reaction, the solid catalyst was separated by vacuum filtration from the reaction mixture, washed with methanol and ether to remove the adsorbed organic compounds and dried at 90 °C overnight for the subsequent cycles. This process was repeated five times.

3. Results and discussion

3.1. Catalyst characterization

The schematic illustration for the preparation of the biguanide-functionalized SBA-15 silica is depicted in Fig. 1. To immobilize 1,2-diisopropyl-4,4,5,5-tetramethylbiguanide onto the surface of SBA-15 silica through a covalent bond linkage, the SBA-15 silica was first surface-modified with 3-chloropropyl-trimethoxysilane as a spacer. Thereafter, the biguanide-functionalized SBA-15 silica was prepared by reaction of the biguanide with 3-chloropropyl-modified SBA-15 silica. The successful immobilization of the biguanide onto the SBA-15 silica was identified by FT-IR spectroscopy, nitrogen adsorption–desorption and elemental analysis techniques.

Fig. 2 shows the FT-IR spectra obtained for SBA-15 silica and biguanide-functionalized SBA-15 silica. For non-functionalized SBA-15 silica, a broad IR absorption band centred at 3460 cm^{-1} appeared mostly owing to framework hydroxyl groups and adsorbed water, and the IR band at 1635 cm^{-1} was ascribed to the bending mode of adsorbed water present in the SBA-15 silica (Nakamoto, 2009). In addition to this, a weak band located at 950 cm^{-1} for the SBA-15 silica was mainly attributed to the stretching vibrations of Si–OH groups at defect sites (Prasetyanto & Park, 2008). Moreover, a series of IR absorption bands at 1080 cm^{-1}, 780 cm^{-1}, and 470 cm^{-1} were observed, which could be assigned to the typical vibration modes of mesoporous framework Si–O–Si (Çıtak, Erdem, Erdem, & Öksüzoğlu, 2012; Prasetyanto & Park, 2008). It was noticeable that the characteristic IR bands of surface hydroxyl groups at 3460 cm^{-1} and 950 cm^{-1} decreased in intensity or disappeared after the organo-functionalization, thus revealing that the hydroxyl groups reacted with the organic groups to form the functionalized SBA-15 material. In particular, in comparison with the SBA-15 support, new IR absorption bands at 2942 cm^{-1} and 2876 cm^{-1} were observed for the biguanide-functionalized SBA-15 sample mostly due to the CH$_2$ asymmetric and symmetric vibration respectively (Çıtak et al., 2012; Kalita & Kumar, 2011). Additionally, the IR bands that appeared at 1581 cm^{-1} and 1412 cm^{-1} could be tentatively ascribed to the C=N and C—N stretching of the biguanines attached to the SBA-15 support (Alizadeha, Khodaeia, Kordestaniaa, & Beygzadeha, 2013). In contrast, these IR peaks were totally absent in the spectrum of non-functionalized SBA-15 silica. Taken together, the aforementioned observations confirmed that the biguanide indeed anchored onto the SBA-15 silica.

The elemental analysis for the organic–inorganic hybrid material showed that the carbon, hydrogen and nitrogen contents were 25.78%, 5.52%, and 10.72%, respectively. There was no C, N or H to be detected on the SBA-15 silica since this support was prepared through a calcination procedure at 550 °C for 6 h. According to the results, the loading amount of biguanide per gram of the SBA-15 silica was equivalent to 1.53 mmol/g, assuming that all the nitrogen elements were in the form of biguanide.

The mesoporosity of SBA-15 silica and biguanide-functionalized SBA-15 silica was examined by nitrogen adsorption–desorption measurement, and the obtained isotherms are shown in Fig. 3. It can be seen that the adsorption isotherms for the two selected samples were of representative type IV isotherm with a H1-type hysteresis loop in accordance with IUPAC classification, which is characteristic of mesoporous materials with ordered pore structures (Çıtak et al., 2012; Prasetyanto & Park, 2008). In addition, the adsorption branch of the isotherm exhibited a steep increase in adsorption at a relative pressure of about 0.65, which resulted from the nitrogen condensation, with uniform pore dimensions and high-ordering of the material. Futhermore, the amount of nitrogen adsorbed on the functionalized SBA-15 silica was shown to be lower when compared to parent SBA-15, mostly owing to a decreased surface area. By drawing on the above results, it is reasonable to conclude that the SBA-15 support still retained its ordered mesoporous structure after the organo-functionalization reaction.

The textural properties are calculated from the N$_2$ adsorption–desorption isotherms at −196 °C. For the SBA-15 support, the average pore size was 6.64 nm, and the measured surface area was as high as 590 m^2/g, in agreement with the literature (Çıtak et al., 2012; Prasetyanto & Park, 2008). The biguanide-functionalized SBA-15 silica possessed a surface area of 276 m^2/g and a pore volume of 0.48 cm^3/g, and it had narrow pore size distribution with an average pore diameter of 5.37 nm. Evidently, the functionalized
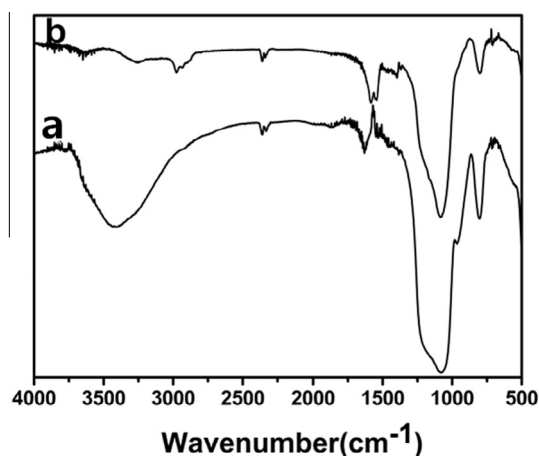

Fig. 2. Fourier transform infrared spectra for samples. (a) SBA-15; (b) SBA-15-pr-biguanide.
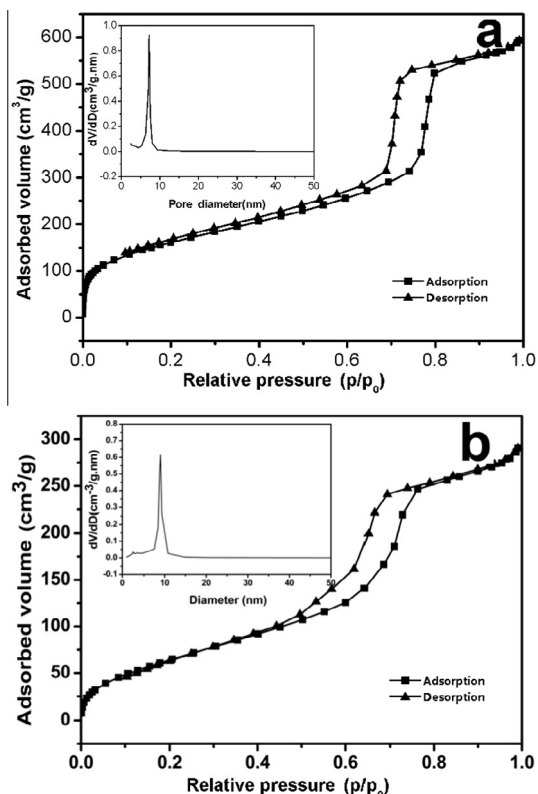
Fig. 3. Nitrogen adsorption/desorption isotherms and pore size distribution profiles (inset) of samples: (a) SBA-15; (b) SBA-15-pr-biguanide.

SBA-15 silica exhibited some loss of surface area and a reduction in pore volume and pore diameter after the organo-functionalization. This phenomenon is considered as a proof that the mesoporous SBA-15 material is functionalized by the biguanide, since the grafting of the biguanide would increase the wall thickness of the SBA-15 support. Despite such a change in the textural properties, the mesoporous structure of SBA-15 silica remained unchanged after the functionalization reaction and the solid hybrid catalyst still possesses relatively large surface area and high pore volume, which are factors in favor of the interesterification reaction.

The low-angle XRD patterns for the SBA-15 silica and biguanide-functionalized SBA-15 silica are displayed in Fig. 1S, Supplementary material. The two samples exhibited a well-resolved XRD peak at 0.91° and two weak peaks at 1.56° and 1.76°, which were indexed as the (100), (110) and (200) reflections, respectively (Çıtak et al., 2012; Prasetyanto & Park, 2008). These obtained XRD patterns show that the two dimensional hexagonal mesoporous structure of SBA-15 silica remained intact even after the functionalization reaction. In addition, the XRD peaks tended to decrease in intensity with the incorporation of organic moieties into the SBA-15 silica, which may be due to the decrease of scattering contrast between the channel walls of the matrices and the covalently bound biguanines in the mesoporous materials (Yue et al., 2008). Moreover, for the functionalized SBA-15 silica, the XRD peaks were shown to shift slightly to higher 2-theta value in comparison with the SBA-15 silica, implying that the reduction of pore size resulted from the incorporation of organic moieties into the mesoporous support (Prasetyanto & Park, 2008). Therefore, it is possible to conclude that the mesoporous structure of the SBA-15 silica is virtually retained after the organo-functionalization reaction. This ordered mesoporous structure can enhance the accessibility of active sites to the reactants and also decrease the mass transfer limit of the feedstocks and the products, facilitating a rapid reaction rate.

The thermal behavior of the biguanide-functionalized SBA-15 silica is presented in Fig. 2S, Supplementary material. There were two major weigh loss regions in the TGA curves. A small amount of mass loss (about 4.2%) ranging from 40 °C to 200 °C with an endothermic event in the DTA curve, could be attributed to the thermal removal of physically held water. With increasing temperature, a significant mass loss between 200 °C and 750 °C (about 61.2%) and a strong endothermic event at about 500 °C appeared. Considering its high endothermic temperature, this main mass loss could principally be attributed to the thermal degradation of the biguanidylpropyl groups attached on the SBA-15 surface. Above 750 °C, almost no mass loss in the TG curve could be observed, suggesting that the tethered organic moiety was totally decomposed at this temperature.

The SEM micrographs obtained for the SBA-15 silica and biguanide-functionalized SBA-15 silica are shown in Fig. 3S, Supplementary material. The SBA-15 silica consisted of many ropelike domains with a uniform size around 1 μm, which were aggregated into a wheat-like macrostructure, in agreement with structures described previously in the literature for conventional SBA-15 materials (Çıtak et al., 2012). Moreover, the biguanide-functionalized SBA-15 silica displayed a similar wheat-like morphology to parent SBA-15 silica. No significant change in the surface morphology occurred after the organo-functionalization except that the domains were more densely packed. In an attempt to gain further insight into the structure of the functionalized SBA-15 silica, the morphology properties were also characterized by TEM techniques (Fig. 4S, Supplementary material). The TEM image of SBA-15 silica clearly revealed the regular hexagonal array of uniform channels, indicative of the presence of a highly ordered pore structure of the SBA-15 material (Kalita & Kumar, 2011; Çıtak et al., 2012). The biguanide-functionalized SBA-15 silica displayed a similar TEM image to the parent SBA-15 silica, which is additional evidence that the ordered hexagonal mesoporous framework is essentially preserved after anchoring of organic moieties onto siliceous SBA-15. The ordered hexagonal mesoporous structure with relatively large surface can ensure efficient reactant diffusion and catalytic site accessibility during the interesterification reaction.

3.2. Interesterification of soybean oil and methyl decanoate

The catalytic activity of the solid hybrid catalyst was firstly evaluated by the interesterification of soybean oil and methyl decanoate. In this study soybean oil and methyl decanoate were chosen as reactants, so as to simplify the interpretation of the interesterification reaction, as well as to produce structured lipids containing medium-chain FAs. The catalytic activity of the tested catalyst was represented by the decanoyl incorporation into the soybean oil.

As expected, by using the SBA-15 silica as a catalyst for the interesterification reaction, no product was obtained, revealing that the unmodified SBA-15 silica had no considerable catalytic activity. After anchoring of the biguanide onto the SBA-15 support, the functionalized SBA-15 silica was found to be active towards the reaction. Over the solid base catalyst, the decanoyl group was indeed incorporated into the virgin soybean oil triacylglycerols and simultaneously the IV value was decreased from 134.2 to 89.3, which showed that the interesterification could practically vary the TAG profiles of the starting oil. The influence of reaction temperature, reaction time, catalyst loading, and substrate ratio on the decanoyl incorporation is illustrated in Table 1.

The substrate ratio exerts a significant effect on the catalytic interesterification. As seen from the data displayed in Table 1, when the substrate molar ratio increased, the decanoyl incorporation showed increasing patterns. It is commonly accepted that an

Table 1
Reaction conditions and results of the interesterification of soybean oil with methyl decanoate catalyzed by SBA-15-pr-biguanide.

Methyl decanoate/soybean oil (molar ratio)	Reaction time (h)	Catalyst amount (%)	Reaction temperature (°C)	Decanoyl incorporation (%)
0.5:1	4	10	90	11.5
1:1	4	10	90	19.8
2:1	4	10	90	27.8
3:1	4	10	90	29.2
4:1	4	10	90	30.5
5:1	4	10	90	31.2
4:1	0.5	10	90	11.8
4:1	1	10	90	15.4
4:1	2	10	90	17.9
4:1	3	10	90	25.6
4:1	4	10	90	30.5
4:1	5	10	90	30.8
4:1	4	1	90	9.7
4:1	4	5	90	12.5
4:1	4	8	90	24.8
4:1	4	10	90	30.5
4:1	4	12	90	29.7
4:1	4	10	50	9.8
4:1	4	10	60	11.2
4:1	4	10	70	17.5
4:1	4	10	80	27.9
4:1	4	10	90	30.5
4:1	4	10	100	30.2

increase in the amount of methyl decanoate could enhance the incorporation of decanoyl moieties in the TAGs by shifting the chemical equilibrium towards the product formation. Thus, a higher substrate ratio is beneficial to the interesterification from the view of reaction equilibrium, resulting in a higher decanoyl incorporation. However, no obvious further increase in the decanoyl incorporation was found when the methyl decanoate/soybean oil molar ratio was increased beyond 4:1. Based on the results, the appropriate methyl decanoate/soybean oil molar ratio is 4:1.

The reaction temperature was set at 50, 60, 70, 80, 90, and 100 °C to elucidate the influence of the reaction temperature on the decanoyl incorporation, and the results are also included in Table 1. When the reaction temperature increased from 50 °C to 90 °C, the decanoyl content was substantially raised from 9.8% to 30.5%. Generally, the higher temperature can facilitate the diffusion of reactants to the surface of the solid catalyst and can also increase the reaction rate, thus leading to the increased decanoyl incorporation. The maximum incorporation of decanoyl groups into the TAGs was attained at 90 °C. However, by further increasing reaction temperature to 100 °C, a slight decline in decanoyl content of the interesterified product was observed. Accordingly, in the present study, the optimum temperature for the interesterification reaction is taken to be 90 °C.

As indicated in Table 1, the decanoyl content was shown to increase from 11.8% to 30.5% as the reaction time increased from 0.5 h to 4 h. However, upon prolonging the reaction time beyond 4 h, no significant change in the decanoyl content occurred, as a result of chemical equilibrium. On the basis of the above results, it can be concluded that the suitable reaction time is 4 h.

The effect of catalyst dosage on the decanoyl incorporation was investigated by modulating the catalyst loading in the reaction, and the results are presented in Table 1. As can be seen, at a low catalyst loading of 1 wt.%, the decanoyl incorporation was only 9.7% owing to insufficient active sites to catalyze the interesterification reaction. With an increase in the catalyst dosage from 1 wt.% to 10 wt.%, the decanoyl incorporation rose from 9.7% to 30.5% due to an increase in the number of active sites available for the reaction. However, a further increase in the catalyst dosage caused a decrease in the decanoyl incorporation. Such a reduction in the

decanoyl incorporation probably resulted from the higher viscosity of the reaction medium with the higher catalyst loading, thus leading to less effective transfer of the substrates to the catalytically active sites. Therefore, the optimum catalyst loading is considered to be around 10 wt.%.

3.3. Interesterification of soybean oil and palm stearin

To expand the scope of its application, the performance of the solid catalyst was further tested in the interesterification of soybean oil and palm stearin. Palm stearin, which is fractionated from palm oil, is usually employed as a material for the interesterification reaction due to its easy availability and lower prices. However, this solid fat does not completely melt at body temperature owing to its high melting point and can cause low plasticity of the end product after the interesterification reaction. For this reason, the soybean oil containing a large amount of polyunsaturated FAs, must be blended and submitted to chemical interesterification in order to impart plasticity to the final interesterified product.

The major FAs in the soybean oil were linoleic acid (53.6%), oleic acid (23.2%), linolenic acid (7.2%), palmitic acid (11.2%), and stearic acid (4.6%). The unsaturated FAs present in the soybean oil accounted for 84% of the total FAs (Silva et al., 2009). Palm stearin contained a high amount of palmitric acid and oleic acid (85.1% and 9%, respectively).

Various blends were prepared for the interesterification reaction by using different proportions of soybean oil and palm stearin. In this way, the total FA compositions of the blends varied depending on the ratios of soybean oil to palm stearin in the blends. Soybean oil can provide a desirable FA composition in term of polyunsaturated FAs, consequently reducing the saturated FAs in the blends. By blending palm stearin and soybean oil, a desirable FA profile could be obtained which has a heath protective effect.

Obviously, the catalytic interesterification did not alter the FA composition of the blends (data not shown), since it only allowed the exchange of FAs between and within the TAGs molecular. Furthermore, no *trans* FAs were detected in the interesterified product. However, the physical and functional characteristics were greatly influenced by the interesterification due to the altered TAG composition.

In the soybean oil, the *sn*-2 position was mainly occupied by linoleic acid (68.4%), oleic acid (24.4%), linolenic acid (5.5%), palmitic acid (1.1%), and stearic acid (0.5%). Clearly, the unsaturated FAs were distributed mainly at the *sn*-2 position of the soybean oil. Meanwhile, the dominant FAs at the *sn*-2 position of palm stearin were palmitic acid and oleic acid (Table 2). Interesterification is commonly employed to modify vegetable oils for the preparation of structured lipids by rearranging the positional distribution of FAs. The profiles of FAs at the *sn*-2 position of the binary mixtures before and after interesterification are shown in Table 2. As observed, for all the blends, the FA profile at the *sn*-2 position was noticeably changed after the interesterification reaction. For instance, for the 40:60 blend of palm stearin and soybean oil, the *sn*-2 positional FA profiles of palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid varied from 30.2%, 1.1%, 22.3%, 43.2%, and 2.7% to 39.7%, 2.3%, 20.2%, 34.8% and 2.3%, respectively. The alteration of positional FA compositions strongly indicated that the interesterification reaction had occurred.

The TAG compositions of palm stearin, soybean oil as well as their blends before and after the interesterification were assessed and the results are listed in Table 3. According to the HPLC analyses, the predominant TAG species present in the soybean oil employed in our study were POO (22.8%), PLL (13.7%), PStO (12.8%), PPO (9.7%), POL (8.9%), PPL (8.6%) and StOL (4.7%), meanwhile palm stearin contained a large amounts of PPP (82.1%), followed by PPO (9.2%), POSt (3.8%) and POO (3.0%)

Table 2

sn-2 positional fatty acid compositions (%) of soybean oil, palm stearin and their blends in various ratios before and after interesterification reaction.

PS/SO ratio	Palmitic 16:0	Stearic 18:0	Oleic 18:1	Linoleic 18:2	Linolenic 18:3	SFA	USFA
Palm stearin	84.6 ± 2.0	4.3 ± 0.2	9.5 ± 0.6	1.2 ± 0.2	1.1 ± 0.1	88.9	10.7
70:30 before	51.2 ± 1.6	1.8 ± 0.4	19.7 ± 0.9	25.6 ± 0.7	1.1 ± 0.2	53.0	46.4
70:30 after	59.2 ± 1.9	2.3 ± 0.1	18.1 ± 0.6	18.4 ± 0.5	1.4 ± 0.2	61.5	37.9
60:40 before	42.8 ± 1.4	1.4 ± 0.4	21.3 ± 0.8	32.1 ± 1.1	1.4 ± 0.2	44.2	55.4
60:40 after	51.6 ± 1.8	2.1 ± 0.6	20.1 ± 0.7	22.8 ± 1.0	2.9 ± 0.3	53.7	45.8
40:60 before	30.2 ± 0.8	1.1 ± 0.2	22.3 ± 0.6	43.2 ± 1.6	2.7 ± 0.2	31.3	68.2
40:60 after	39.7 ± 1.3	2.3 ± 0.4	20.2 ± 0.8	34.8 ± 1.1	2.3 ± 0.2	42.0	57.3
30:70 before	24.5 ± 0.8	1.2 ± 0.1	23.6 ± 0.6	47.8 ± 1.3	2.4 ± 0.3	25.7	73.8
30:70 after	33.2 ± 0.9	3.4 ± 0.3	20.5 ± 0.5	39.4 ± 1.1	3.1 ± 0.1	36.7	63.0
Soybean oil	1.3 ± 0.3	0.5 ± 0.1	22.3 ± 1.3	69.2 ± 1.2	6.3 ± 0.5	1.8	97.8

PS-palm stearin; SO-soybean oil; SFA-sum of saturated fatty acid; SUFA-sum of unsaturated fatty acid.

Table 3

Triacylglycerol composition (percent) of soybean oil, palm stearin and their blends in different ratios before and after interesterification reaction.

TAG	PS	70:30		60:40		40:60		30:70		SO
		Before	After	Before	After	Before	After	Before	After	
LLLn	0.0	1.3	0.7	1.9	1.3	2.4	2.1	3.3	2.5	7.4
LLL	0.0	5.1	2.6	7.4	4.2	12.6	5.4	17.8	12.3	26.6
OLnL	0.0	0.4	0.5	0.9	1.1	1.2	1.1	0.8	1.2	2.9
OLL	0.0	4.6	3.8	6.4	4.8	9.2	7.0	13.6	10.4	18.9
PLL	0.0	3.7	7.4	5.5	8.5	7.1	10.8	11.2	14.1	16.1
OLO	0.0	2.5	1.7	3.2	3.3	4.1	3.1	5.6	4.5	7.4
PLO	0.0	4.0	5.8	4.2	8.7	6.2	13.6	7.2	12.9	11.6
PPL	0.0	0.3	5.3	0.6	8.5	0.8	11.3	1.1	6.3	1.5
StPL	0.9	1.2	2.6	1.5	2.1	1.1	2.7	1.5	5.1	1.7
POO	2.7	3.2	5.6	2.6	8.3	3.4	6.5	2.8	4.1	3.9
PPO	8.7	8.3	11.2	6.7	9.1	4.3	7.6	3.1	5.2	1.2
PPP	83.2	62.3	50.4	56.3	38.2	45.2	26.2	30.6	19.8	0.0
PPSt	0.4	0.4	0.5	0.2	0.3	0.6	0.6	0.1	0.2	0.5
POSt	3.8	2.1	1.1	1.6	0.8	0.9	0.8	0.5	0.4	0.2
StOO	0.0	0.2	0.4	0.5	0.4	0.4	0.9	0.2	0.5	0.3

TAG-triacylglycerol; PS-palm stearin; SO-soybean oil; P-palmitic acid; St-stearic acid; L-linoleic acid; O-oleic acid; Ln-linolenic acid.

(Adhikari et al., 2010; Lee, Su, Lee, & Lin, 2013). As illustrated in Table 3, different TAG profiles of the blends were achieved according to the starting blends with different ratios of palm stearin to soybean oil. More importantly, as compared to initial blends, the interesterified blends showed an obvious variation in the TAG species after the interesterification reaction. In particular, for the 40:60 blend of palm stearin and soybean oil, the proportions of TAG species, such as PPP, OLO, OLL, LLL, and LLLn were reduced from 45.2%, 4.1%, 9.2%, 12.6%, and 2.4% to 26.2%, 3.1%, 7.0%, 5.4%, and 2.1%, after the interesterification, and concomitantly the proportions of some other TAG species, such as PPO, POO, StPL, PPL, PLO and PLL were observed to increase from 4.3%, 3.4%, 1.1%, 0.8%, 6.2% and 7.1% to 7.6%, 6.5%, 2.7%, 11.3%, 13.6%, and 10.8%, respectively. Such obtained results show that the substantial change in TAG species occurred after the catalytic interesterification reaction, implying that the FAs were rearranged within and between TAG backbones during the interesterification process catalyzed by the solid catalyst. The change of TAG species resulted from the redistribution of the FAs.

Soybean oil is always in a liquid state due to the large proportion of unsaturated FAs. The altered TAG composition of the interesterified blends caused by the interesterification was also reflected by changes in the melting point (Table 1S, Supplementary material). The physical blends displayed a wide range of SMPs (47.6–50.6 °C). However, SMPs of the interesterified products tended to be reduced compared to those of the physical blends (Table 1S, Supplementary material). The observed change of the SMPs after the interesterification was accompanied by the change of the TAG compositions. Fats with SMPs lower than body temperature can be employed as shortenings, since this fat melts completely in the mouth and produces no waxy sensation.

3.4. Reusability of the catalyst

The recyclability is an important factor when considering use of a heterogeneous catalyst in practical applications. The reusability of the solid catalyst was assayed for the interesterification of soybean oil and methyl decanoate in repeated batches carried out under the same reaction conditions as described above. As the catalyst was used for 1, 2, 3, 4, 5 cycles, the decanoyl incorporations over the recovered catalyst were 30.5%, 29.6%, 29.1%, 27.6%, and 21.5% respectively. It was shown that the catalytic activity decreased as the recycling time increased, which was probably due to the accumulation of organic or carbonaceous materials on the catalyst surface (Léon et al., 2015). No significant decrease in the catalytic activity was observed for 4 cycles of reuse. However, upon the fifth cycle, the recovered catalyst displayed a marked loss of the activity.

To further prove the heterogeneous behavior of the solid catalyst, an additional test was performed, in which the catalyst was separated from the reaction mixture after 2 h of reaction and then the reaction was processed for another 3 h. The results showed that no further decanoyl incorporation was observed at the extended reaction time, indicating that there was no reaction in the liquid phase and the reaction process was essentially heterogeneous.

4. Conclusions

An efficient solid base catalyst, namely a biguanide-functionalized SBA-15 silica with a mesoporous structure, was prepared by grafting the organic biguanide onto the SBA-15 material.

The catalyst characterization results showed successful anchoring of the biguanide on the SBA-15 materials, and the highly ordered mesoporous structure of SBA-15 silica remained almost unaltered after the organofunctionalization. The inorganic–organic hybrid materials, prepared in this way, can be utilized as efficient heterogeneous catalyst for the interesterification reaction. The catalyst could be easily separated and reused several times without significant activity loss. By using this catalyst, a feasible eco-friendly process to modify vegetable oils has been developed.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2015.10.103.

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