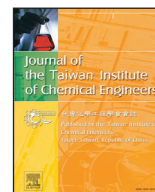




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Valorization of biodiesel plant-derived products via preparation of solketal fatty esters over calcium-rich natural materials derived oxides

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ABSTRACT

The use of lipid derived components as a raw material for the preparation of solketal fatty esters via heterogeneous catalysis route is the main objective of this work as an attempt to maintain the sustainability of biodiesel production industries. Oxides derived from highly abundant and low cost calcium-rich natural materials, including dolomite, seashell, chicken eggshells and cuttlebone, by simple calcination were investigated as solid base catalysts for the transesterification of methyl decanoate with solketal under solvent free conditions. Among the catalysts studied, the calcium and magnesium mixed oxides derived from dolomite gave the highest yield (84%) of solketal fatty esters at 150 °C within 6 h and their superior catalytic activity was correlated with their higher basicity. The catalyst could be regenerated by calcination at 800 °C and successfully reused for up to five cycles with <20% drop in the catalytic activity. The formation of calcium fatty ester hydrates, as soap-like compounds, during the catalytic reaction caused a loss of active calcium species. Under the optimized conditions, transesterification of various fatty acid methyl esters (FAMES) with solketal was characterized and revealed that long-chain FAMES were preferential reactants.

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1. Introduction

The utilization of non-renewable fossil fuels results in huge environmental problems that created awareness to look for some alternative and sustainable energy sources [1]. Biomass is one of the renewable sources and is actively in progress for energy and chemical production all over the world [2]. Vegetable oils and animal fats, so-called lipids, come under the category of biomass and have gained significant industrial interest because of their competitive cost, wide availability and their functionality. Tremendous number of studies has been performed on the preparation of biodiesel by the transesterification reaction, where ~10 wt% of glycerol is produced as a by-product [3]. Lipid-derived fatty compounds and glycerol are basic oleochemicals potentially used as the raw materials for the preparation of numerous specialty chemicals and value-added products, such as lubricants, fuel additives, dyes, solvents, fragrance, cosmetics, polymers, etc. [4,5].

It is expected that the continuous production of biodiesel to (partially) replace petroleum diesel fuels will lead to an enormous amount of glycerol as bio-waste [6]. The acetalization of glycerol with aldehyde and ketone gives acetals and ketals, which have applications in the formulation of gasoline, diesel and biodiesel fuels for improving their fuel properties [7]. Solketal is a simple acetal molecule prepared by the reaction of glycerol with acetone using acid catalysts [7–9]. The presence of free –OH groups in solketal allows it to function as an alcohol source for the preparation of solketal fatty esters (SFE) via base-catalyzed transesterification with fatty acid methyl esters (FAMES) [10] (Scheme 1). In an alternate method, SFE can also be prepared by the catalytic esterification of fatty acids with solketal in the presence of immobilized lipases [11] and *p*-toluenesulfonic acid [12]. The SFE obtained can be used as fuel additives, lubricants, solvents, flavoring agents, plasticizers, etc. This transformation uses primary (FAMES) and secondary (glycerol-derived solketal) lipid derivatives as the raw materials, and thus possibly creates a new path to oleochemical industries and increases the sustainability of biodiesel industries.

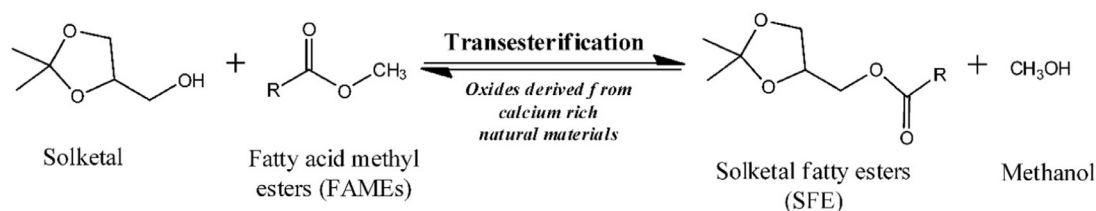
Development of highly active, stable and low-cost heterogeneous catalysts is in demand for economical and eco-friendly biodiesel production processes. Calcium-rich natural materials are available in surplus and are accepted as very cheap feedstocks [13].

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Scheme 1. Transesterification of FAMEs with solketal to produce solketal fatty esters.

However, some of these materials, such as eggshells and mollusk shells, are discarded in landfills as waste materials without any alteration [14], which generate environmental pollution and also health problems to humans due to their odor and biodegradation [15]. Studies have already been reported on the utilization of these natural materials and their modified forms as adsorbents [16,17], sources for biomaterials [18,19], biosensors [20] and active catalysts [21,22]. Dolomites are naturally abundant mixed calcium–magnesium carbonate rocks that are formed by the substitution of magnesium for calcium in the limestone [23]. Seashells and eggshells are the protective outer layer (shell) of sea animals and animal eggs, respectively, whereas cuttlebone is an internal shell of the cuttlefish, and all these materials are rich in calcium carbonate. Recently, the calcium-rich natural materials have gained in interest in the field of base catalysis for the biodiesel production via the transesterification of lipids with alcohols due to their availability, high purity, low toxicity, simple processing steps and easy modifications as per requirements [23–28]. Furthermore, these types of catalytic materials are highly recyclable and more environmental friendly than conventional alkali bases.

To the best of our knowledge, this work is the first report on the preparation of SFE via heterogeneously catalyzed transesterification. As an attempt toward more environmentally benign and sustainable process, the oxides derived from various calcium-rich natural sources, including dolomite, seashell, chicken eggshells and cuttlebone, were applied as heterogeneous base catalysts for the transesterification of methyl decanoate with solketal under solvent free conditions. Further detailed characterizations of the active and spent catalysts, parametric variation, reusability and different FAMEs substrate variation studies were discussed.

2. Materials and methods

2.1. Materials and chemical reagents

Solketal (>97%), methyl oleate (>85%), *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA; >99%), methyl undecanoate (C₁₁ FAME; 99%) were purchased from Sigma-Aldrich. Commercial methyl decanoate (C₁₀ FAME; >97%) and a C₈–C₁₀ FAMEs mixture were provided by the Thai Oleochemicals Co., Ltd., Thailand. Palm biodiesel was prepared in the laboratory following the reported procedure [29]. The composition of the different FAMEs used in this study is given in the Supplementary Material (SM) Table S1. Toluene (AR grade) was purchased from QREc.

2.2. Catalyst preparation

All of the calcium-rich natural materials were ground in a mortar and sieved to reduce the particle sizes to less than 40 μm diameters before being used as catalyst precursors. The powdered materials were then calcined in a muffle furnace at 800 °C for 3 h with a heating rate of 10 °C/min. The furnace temperature was then decreased to 200 °C and upon reaching that temperature the calcined materials were immediately transferred into a tightly packed container and kept in a desiccator in order to prevent contamination

by atmospheric moisture and CO₂. In all the reactions, freshly calcined materials were used. The starting natural materials and their corresponding oxide catalysts were named as XX and XX_{oxide}, respectively, where XX indicates the name of the materials.

2.3. Catalyst characterization

The elemental composition of the powdered calcium-rich natural materials was analyzed by energy dispersive X-ray fluorescence spectrometry (XRF) using a JEOL ED-2000 X-ray fluorescence spectrometer. Powder X-ray diffraction (PXRD) was performed on a Bruker D8 ADVANCE X-ray diffractometer with Cu Kα radiation operating at 40 kV and 40 mA. The PXRD patterns were recorded at room temperature at a step size of 0.02° over a 2θ range of 5–80°. The identification of crystalline structures was made by consulting the Joint Committee on Powder Diffraction Standards (JCPDS) files and the corresponding crystallite sizes were calculated using the Debye-Scherrer equation. Thermogravimetric analysis (TGA) was used to determine the thermal decomposition of the starting materials and the spent catalysts using a PerkinElmer Diamond thermogravimeter. The weight loss and derivative thermogravimetric (DTG) curves were recorded from 50 to 800 °C at a temperature ramp rate of 8 °C/min under a nitrogen (N₂) flow (50 mL/min).

The basic strength of the catalysts was determined using the Hammett indicator method with methyl red (pK_a = 4.8), neutral red (pK_a = 6.8), bromothymol blue (pK_a = 7.2), phenolphthalein (pK_a = 9.8) and 2,4-dinitroaniline (pK_a = 15.0). The total basicity of the catalysts was determined by acid–base titration using phenolphthalein as the indicator [30]. In a typical method, 25 mg of freshly calcined sample was suspended in 10 mL of 5 wt% phenolphthalein in methanol solution. The resulting mixture was stirred well for 30 min at room temperature, and then titrated with 0.01 M benzoic acid in methanol.

Temperature-programmed desorption of carbon dioxide (CO₂-TPD) was applied to determine the basic properties of the catalysts using a Micromeritics AutoChemII 2920 chemisorption analyzer. The freshly calcined catalysts were pretreated at 400 °C for 1 h under a helium (He) flow (50 mL/min), after which the adsorption of CO₂ (10% (v/v) in He) was performed at 100 °C. The CO₂ physisorbed on the catalysts was purged with He at the same temperature for 30 min. The temperature was then increased to 900 °C at 10 °C/min for desorbing CO₂.

The textural properties of the catalysts were measured by N₂ physisorption using a Micromeritics ASAP 2020 surface area and porosity analyzer. The samples were degassed at 300 °C for 2 h prior to the measurement. Calculation of the specific surface area was based on the Brunauer–Emmett–Teller (BET) equation using the linear-relationship data attained in the relative pressure (*P*/*P*₀) range of 0.02–0.2. The morphology of the starting materials and the spent catalysts was observed by scanning electron microscopy (SEM) using a JEOL JSM-5410 LV scanning electron microscope. The samples were first sputter coated with gold and then analyzed at an accelerating voltage of 15 kV with magnification ranges from 100× to 20,000×.

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