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Solvent free synthesis of methyl palmitate over sulfated zirconia solid acid catalyst

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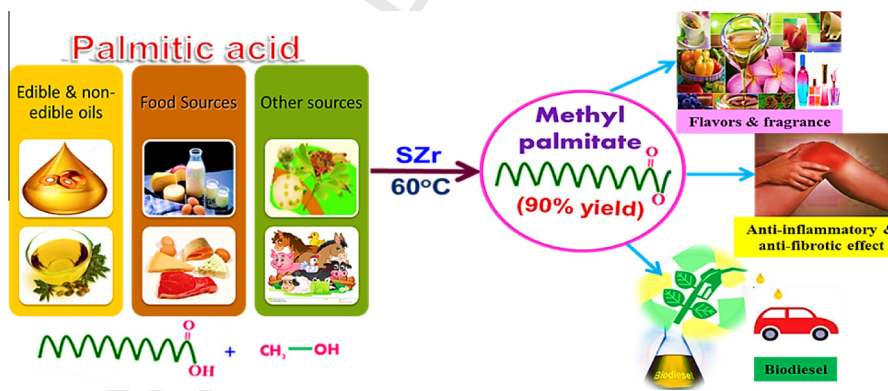
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HIGHLIGHTS

- SZr solid acid catalyst prepared by simple precipitation method and characterized.
- Excellent activity for esterification of palmitic acid with methanol.
- Higher yield of methyl palmitate under solvent free and mild reaction condition.
- Yield of alkyl palmitate decreased with methanol to *n*-butanol.
- Activity comparable with H₂SO₄, though decreased in re-cycling due to sulfur loss.

GRAPHICAL ABSTRACT

The esterification of palmitic acid with methanol resulted into 90% yield of methyl palmitate at 60 °C over 6 wt% of conventional sulfated zirconia catalyst under solvent-free conditions.



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ABSTRACT

Sulfated zirconia (SZr) solid acid catalyst, prepared by conventional precipitation technique was studied for esterification of palmitic acid with methanol to synthesize methyl palmitate. The catalyst exhibited 90% yield of methyl palmitate at 60 °C over 6 wt% catalyst. The yield was significantly higher under solvent-free conditions than using hexane as a solvent. The alkyl palmitate yield was decreased with an increase in the alkyl chain of alcohol from methanol to *n*-butanol. The reaction followed pseudo-first order kinetics under the optimized reaction conditions with a reaction rate of 0.61 mmol h⁻¹, rate constant of 12.13 × 10⁻³ h⁻¹ and turn over frequency of 0.088 min⁻¹.

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1. Introduction

The fatty acid alkyl esters are widely used in the production of fuel, cosmetics and detergents in the chemical industry. In the last decade, esterification of long chain fatty acids with short chain alcohol has spurred to the scientific community with the

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emergence of biodiesel as a promising renewable energy source [1]. Biodiesel consists of mixture of methyl or ethyl fatty acid esters resulting either from the esterification of fatty acids using acid catalysts or the transesterification of oil with base catalysts. Though the production of biodiesel via transesterification of oils with conventional base catalysts is commercialized, the esterification of low-cost feedstock such as non-edible oils and animal fats having higher free fatty acid contents is an essential step to avoid soap formation that reduces the biodiesel yield [2]. There are four methods namely acid catalyzed esterification [3], steam injection [4], chromatography [5] and film vacuum evaporation [6] for removing free fatty acids from low-cost feedstock. Among the different possible methods, the esterification method is advantageous over the other methods as it directly yields fatty esters [1,7]. Among various saturated fatty acids, palmitic acid (C₁₆H₃₂O₂) is present in all edible and non-edible oils in varying amount (4–23%). It is one of the major components (48%) of palm oil among total saturated fatty acids (54%) [8] that is used to produce methyl palmitate, a significant component of biodiesel. Methyl palmitate is also used in flavors and fragrance and biologically has anti-inflammatory and anti-fibrotic effect [9].

Conventionally, homogenous acid catalysts including strong Brønsted mineral acids (e.g. sulfuric or hydrofluoric acid) and *p*-toluenesulfonic acid have been used for esterification reaction. However, these acids lead to serious contamination and corrosion problems and require neutralization before disposal of waste and purification of the product [10,11] and thus homogeneous acid-catalyzed systems are not a good choice for commercial applications [12]. Therefore the extensive demand for cleaner methodologies emerged eco-friendly heterogeneous acid catalysts that can be easily separable and re-usable.

A number of solid acid catalysts have been studied for the esterification of fatty acids [13–15], intensive efforts are still going on to search a better catalyst. The solid acid catalyst should have low cost, necessary strong acid sites, high activity and selectivity for desired product at mild reaction conditions of low acid/alcohol ratio, catalyst amount and temperature. Several reports on the esterification of palmitic acid showed that various solid acid catalysts such as WO_x loaded on ZrO₂ [16] and ZrPO₄ [17], sulfonated carbon and chitosan [18], silica supported heteropolyacid [19], MCM-41 [20], silica [21] or niobia [22] supported and ammonium salt [23] of 12-tungstophosphoric acid were found to have good catalytic activity; however, appreciable yields of methyl palmitate could be achieved at higher acid to methanol ratio (1:30 to 1:270) [17,18,20,22–24], reaction temperature (64–200 °C) [23,25,26] and reaction time of 24–30 h [17,21] over 10–100 wt% catalyst [21,24–27]. The undesirable by-product namely dialkyl ethers are also formed due to etherification reactions under harsh reaction conditions [28]. These stringent conditions are not favorable from economic and industrial point of view. Besides these catalysts, only few studies have been reported for esterification of palmitic acid on SZr solid acid catalyst [27,29]; however higher acid to methanol ratio (1:40) and catalyst amount (15 wt %) are reported to obtain 89–97% conversion of palmitic acid at 60–95 °C temperature. SZr incorporated in SBA-15 has also been reported to exhibit 89% conversion at 68 °C with a higher acid to methanol ratio of 1:80 [29].

Herein, we report a systematic study of esterification of palmitic acid with methanol at lower acid to methanol ratio over SZr catalyst, prepared by simple conventional method. The effects of various reaction parameters such as acid to alcohol molar ratio, catalyst amount, reaction temperature, time, stirring speed along with other short chain alcohols namely ethanol, *n*-propanol and *n*-butanol have been studied. The re-cycling of SZr catalyst and important factors leading to its deactivation during its re-cycling has also been addressed.

2. Experimental

2.1. Catalyst synthesis

SZr catalyst was prepared using a conventional precipitation technique as described previously [30a]. In a typical synthesis procedure, aqueous solution of ZrOCl₂·8H₂O (s.d.fine-chem. Ltd.) was hydrolyzed by drop-wise addition of aqueous ammonia (25%; Rankem, India) under continuous stirring until the pH became 10. The precipitates were filtered, washed with distilled water until free from chloride ions (checked by AgNO₃ solution). The catalyst was dried in an oven at a temperature of 110 °C for 12 h and treated with H₂SO₄ (1 N, 15 ml/g) for 30 min followed by calcination at 600 °C for 4 h.

2.2. Catalyst characterization

2.2.1. Structural, textural and morphological properties

The crystallinity and the crystalline phase of prepared SZr catalyst was determined by X-ray powder diffractometer (Philips X'pert, The Netherlands) using Cu K α radiation ($\lambda = 1.54059 \text{ \AA}$). The crystallite size was determined from the characteristic peak of tetragonal phase of zirconia ($2\theta = 30.3^\circ$) using Scherrer formula [31]. FT-IR spectrum of the catalyst was recorded by FT-IR spectrophotometer (Perkin Elmer, GX, USA) in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹ as KBr pellets. The bulk sulfur (wt%) retained in calcined catalyst was analyzed by elemental analyzer (Perkin Elmer 2400, USA).

Specific surface area, pore volume and pore size distribution of the catalyst was determined from N₂ sorption isotherms at –196 °C (ASAP 2010, Micromeritics, USA). Surface area and pore size was calculated by BET (Brunauer–Emmett–Teller) equation and BJH (Barrett–Joyner–Halenda) method, respectively. The sample was degassed under vacuum (1×10^{-3} mm Hg) at 120 °C for 4 h, prior to adsorption measurement to evacuate the physisorbed moisture.

The microscopic study was done by SEM and TEM micrographs that were obtained using a scanning electron microscope (Leo series VP1430, Germany) and a transmission electron microscope (Jeol JEM 2100, USA), after dispersing the catalyst sample in ethanol by sonication and deposited on an Al grid coated with gold using a Polaron Sputter Coater (for SEM) and on a Cu grid coated with carbon film (for TEM).

2.2.2. Acidic properties

The total surface acidity of the catalyst was measured by temperature programmed desorption (TPD) of NH₃ (Micromeritics Pulse Chemisorb 2720) by standard procedure as described earlier [30b].

Brønsted and Lewis acid sites were differentiated using pyridine as a probe by FT-IR spectrophotometer (Perkin Elmer, GX, USA) equipped with Diffuse Reflectance FT-IR (DRIFT) accessory (Graseby Specac, P/N 19900) and an automatic temperature controller (Graseby Specac, P/N 20130) as described earlier [32]. The quantification of B and L acid sites ratio (B/L) was done from the characteristic peak area of 1545 cm⁻¹ for B and 1442 cm⁻¹ for L at 150 °C as well as by molar extinction coefficient method (using $\epsilon_B = 1.67 \text{ cm}^2/\mu\text{mol}$ and $\epsilon_L = 2.22 \text{ cm}^2/\mu\text{mol}$) [33,34].

Vapor phase cyclohexanol dehydration to cyclohexene in a fixed bed reactor was used as a model reaction to assess the Brønsted acidity of the catalysts. Cyclohexanol (2 ml) was delivered by a syringe pump injector (Cole Parmer, 74900 series) with a flow rate of 1 ml h⁻¹ under N₂ at 175 °C over the catalyst sample (0.2 g) (*in situ* activated at 450 °C for 2 h) packed in a reactor bed. Product samples were collected after 1 h and analyzed with a Hewlett–Packard

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