

Esterification of palmitic acid in sunflower oil using solid acid catalysts

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Introduction

The transesterification of the triglycerides contained in vegetable oil with methanol to yield fatty acid methyl ester (FAME, biodiesel) is homogeneously catalysed by NaOH and KOH bases. Free fatty acids (FFA) are a poison to the catalyst, and also lead to soap formation. The FFA content is low (<1 wt.%) in refined oil, but can exceed 10 wt.% for some crude and recycled oils and greases. The esterification of FFA with CH₃OH using a solid catalyst prior to the esterification reactor is a promising method to convert FFA into valuable FAME [1]. Many solid acids display an activity for the esterification of short carboxylic acids and alcohols [2-5], but deactivate upon reuse [2]. There is also a lack of data on the esterification of long-chain FFA in realistic reaction media (i.e. oils). Therefore, this work aimed at determining active and durable solid catalysts for the esterification of palmitic acid (PA, C₁₆H₃₂O₂) in sunflower oil.

Materials and Methods

The catalysts, i.e. sulfated (SZ, Aldrich) and tungstenated zirconia (MELCat, X20861/02), silica-alumina (Davicat, CL5600) and Nafion/SiO₂ (SAC-13 from Aldrich), were typically calcined at 600°C, except for the SAC-13, which was used as received 30 ml of commercial sunflower oil (Tesco brand) containing 10 wt.% of PA (Aldrich, 99% purity) was placed into a round bottom flask fitted with a reflux condenser. No organic solvent was used. 9 ml of methanol mixed with a known amount of catalyst was then added to the oil. The reaction mixture was stirred at 1000 rpm to increase the dispersion of the reactants, as those were not fully miscible at the temperature used (around 60°C). Contrary to the case of experiments realised at high dilution in an organic solvent [2,4] or in pure FFA medium [5] (in which methanol is fully soluble), the lack of full miscibility constitutes a challenge in the type of work reported here. Samples were collected at regular intervals and the PA content was titrated with a solution of KOH in ethanol.

Results and Discussion

The SZ and the SAC-13 were the most active catalysts under our conditions (60°C: TOF were 0.24 and 0.16 min⁻¹, respectively) and received further attention. The SZ was essentially not active if not calcined above 400°C before reaction. An in situ diffuse reflectance FTIR study of the activation of the SZ revealed that the higher calcination temperatures are necessary to form the highest proportion of a band at 1403 cm⁻¹, which is associated with the presence of highly covalent surface sulfate species [6]. The effect of the reactants and reaction products of the esterification were investigated over the activated SZ. Neither the methanol nor the mixture oil+palmitic acid had any deleterious effect on the activity. This indicates that SZ can actually be stored in the alcohol or the oil once activated. On the contrary, water almost fully inhibited the activity of the catalyst. Recycling experiments also showed that leaching of sulfate occurred, in agreement with earlier reports [3]. The SZ showed a marked loss of activity with the first recycling, and thereafter a slower gradual loss (Fig. 1, right). The SZ could not be fully regenerated by calcination at 500°C, probably because of the carbon residues derived

from adsorbed oil. As a matter of fact, calcination of SZ following exposure to various reaction mixtures showed that all oil-containing mixtures led to poor activity (Fig. 1, left). The SAC-13 did not deactivate upon reuse and required no activation and therefore appears as a most promising catalyst for the esterification of FFA in oil. The origin of these observations may lie in the hydrophobicity of the SAC-13, which favours water removal away from the catalyst and the sulfonic acid group [2,4]. It is interesting to note that the SAC-13 used elsewhere with various carboxylic acids up to C₈H₁₆O₂ (in the presence of a large excess of tetrahydrofuran solvent) exhibited a marked deactivation upon each reuse cycle [2]. The origin of this discrepancy probably lies in the different nature of the reactants and/or reaction media used.

Significance

Nafion/SiO₂ appears as an active and durable heterogeneous catalyst for the esterification of FFA with methanol in oils, requiring no activation before use. This catalyst could be used in a fixed bed reactor for a cost-effective pre-treatment of FFA-rich oils for biodiesel production.

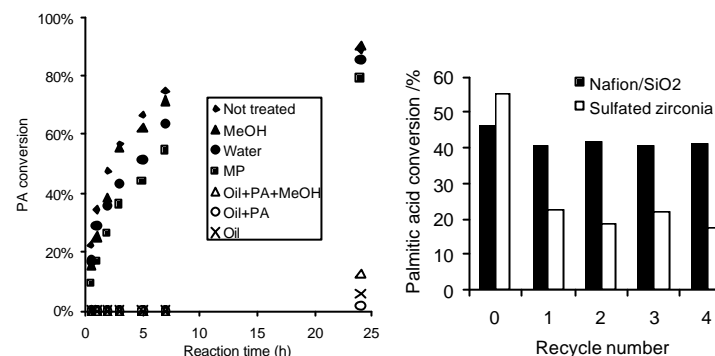


Figure 1. Left: Effect of various pre-treatments followed by a calcination at 500°C on the activity of activated SZ for the methanol-esterification of PA in sunflower oil. Catalyst loading: 3 wt.%. Reaction temperature = 60°C.

Right: Conversion of PA after 3h over SZ and Nafion/SiO₂ (SAC-13) over a number of recycled uses. Catalyst loading = 3 wt.%. Reaction temperature = 65°C.

References

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