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Activity and stability of polyaniline-sulfate-based solid acid catalysts for the transesterification of triglycerides and esterification of fatty acids with methanol

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ABSTRACT

A polymeric catalyst, polyaniline-sulfate, was studied in the transesterification of triglycerides (triacetin, castor oil) and esterification of fatty acid, ricinoleic acid with methanol at mild conditions (temperature of 50–60 °C). Polymer powder (PANI-S) and three samples of various contents of polymer deposited on carbon support were examined. The samples of catalysts, before and after catalytic tests were characterized by BET, FT-IR, XRD and SEM techniques. The acid capacity was also determined. All the samples were found to be active solid acid catalysts in both tested reactions. Catalytic performance of polyaniline-sulfate-based catalysts for methanolysis of triacetin (glycerol triacetate) the shortest triglyceride molecule differed from that for vegetable oil, castor oil, consisting of long chain triglycerides of ricinoleic acid. In transesterification of triacetin PANI-S powder was more active than carbon-supported catalysts. In methanolysis of vegetable oil the outermost surface of catalysts was mainly involved and much higher activity was exhibited by carbon-supported catalysts with deposited polymer, especially with low content of polymer (13.1 wt.%). The activity of polyaniline-sulfate-based catalysts was almost stable during recycling use in tested reactions. After five successive catalytic runs, their activities were found to be ca. 80–95% relative to the activities of fresh catalysts.

1. Introduction

Biodiesel fuel, an alternative to classic diesel fuel, belongs to ecological fuels because it consists of methyl esters of fatty acids, derived from vegetable oils or animal fats. Methyl esters are obtained by the transesterification of triglycerides with short-chain alcohols, such as methanol, as illustrated in Scheme 1. The reaction is catalysed by strong acids or bases, but owing to environmental, technological, and economic reasons, the substitution of industrial homogeneous catalysts by heterogeneous catalysts is a desirable goal.

The advantage of solid acid catalysts consists in the ease of product separation, recycling of the catalyst and reduced equipment corrosion. Solid acid catalysts can be used in a packed bed continuous flow reactor, simplifying the product separation and purification. Moreover, solid acid catalysts are able to catalyse both transesterification of triglycerides and esterification of free fatty acids present in oil feedstock. A variety of solid acids have already been tested for methyl ester synthesis via both, esterification of free fatty acid and transesterification of triglycerides. Their catalytic efficiency has been reviewed in recently published papers [1–5]. The catalysts based on sulfonic groups were found to be the most active in methyl ester synthesis. Two types of solid catalysts are mainly studied: sulfonic acid-functionalized organic resins and sulfate treated inorganic oxides, such as SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2 SO_4^{2-}/SnO_2 [6–8]. They offered a high activity but strongly deactivated because sulfate groups easily leach from these catalysts in contact with reaction mixture which, in turn, gives rise to a homogeneous acid catalysis. On the contrary, non-sulfated superacid material, WO_3/ZrO_2 exhibited good acid properties and high stability, but its activity was lower compared to sulfate-containing oxides [9,10]. The activities of sulfated mixed titania–zirconia oxides when used in fixed bed reactor were as high as that of WO_3/ZrO_2, and they exhibited a very good stability, being only slightly deactivated during long reaction time [11,12]. Heteropolyacids ($H_3PW_{12}O_{40}$) supported by zirconia, silica, alumina, activated carbon [13] and Ta_2O_5 [14] were also tested, however, they are easily deactivated especially in the presence of small quantities of water. By enhancing hydrophobicity of Ta_2O_5/SiO_2 support via functionalization with alkyl groups the activity and stability of catalysts increased [14]. Sulfonic acids-based ion-exchange resins are another class of solid acid catalysts known to be very effective in numerous industrial reactions, including olefin isomerizations, alkylations, acylations,

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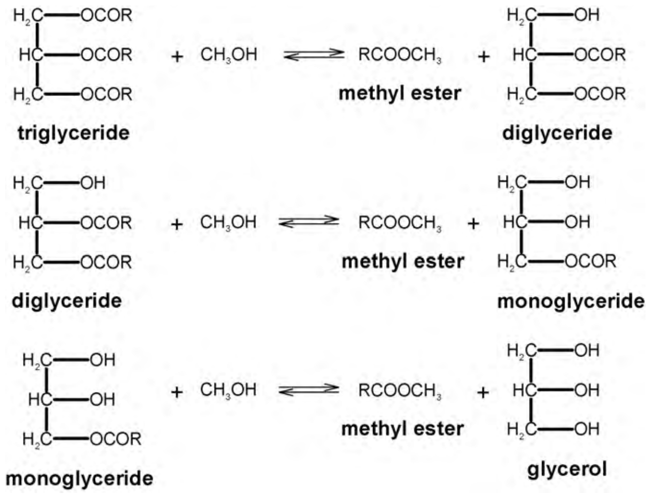


Scheme 1. Transesterification of triglyceride with methanol.

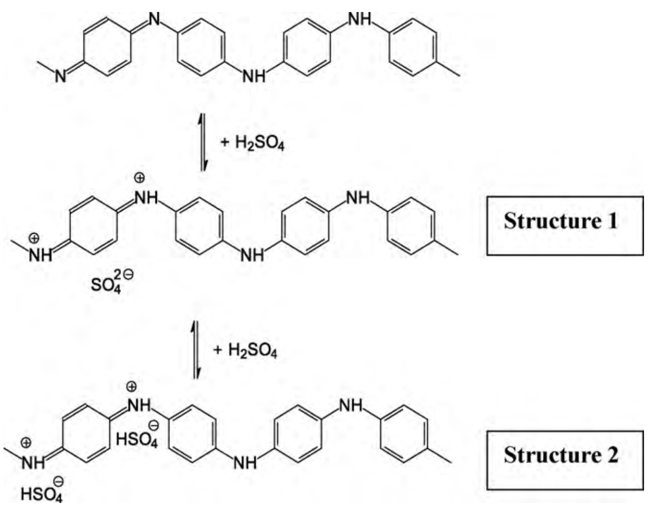
esterifications and others [15]. Two main classes of ion-exchange resins, namely styrene-based sulfonic acids (Amberlyst and Dow type resins) and perfluorosulfonic acid-based catalysts including Nafion resin and Nafion resin–silica nanocomposites such as Nafion SAC-13 [5,15] have been reported to display excellent catalytic activity in esterification of small organic acids and fatty acids to produce methyl esters [16]. Recently, systematic study dealing with catalytic behaviour of different (polystyrene-divinylbenzene) PS-DVB-based sulfonic acid-containing resins in the esterification of fatty acids performed as the pre-step prior to the transesterification of triglycerides was reported [17]. Low thermal stability of Amberlyst-series resins, however, limited the utility of these catalysts for maximum operating limit ca. 120 °C. Catalytic performance of this kind of resin (like Amberlyst, Nafion NR50) was affected by their swelling in reaction mixture which determined the number of sites available for the reactants [7,18,19]. In addition, the activity of Amberlyst-15 significantly decreased after recycling in triacetin methanolysis (at 60°) which was ascribed to site blockage by adsorbed reagents, like more polar intermediates or products [7].

de Rezende et al. [20] demonstrated that activity of sulfonated poly(styrene-co-divinylbenzene) (poly(S-DVB)-SO_3H) and poly(divinylbenzene) (poly(DVB)-SO_3H) catalysts in transesterification of Brazilian vegetable oils (at 65 °C) was higher than that of commercial Amberlyst-15 and Amberlyst-35. The best performance was exhibited by (poly(DVB)-SO_3H) that presented macroporous structure and high surface area. Its activity was comparable to that of p-toluenesulfonic acid and even higher than that of H_2SO_4 under homogeneous conditions. No data of reusing the catalysts were reported. Sulfonated polystyrene-based catalysts prepared from linear polystyrene were reported by Soldi et al. [21] to be more efficient than Amberlyst-15 in transesterification of refined soybean oil and beef tallow (at 64 °C) and high excess of methanol (100:1). A significant reduction in their activity observed under recycling use was attributed to the impregnation of polar compounds such as glycerol, partial glycerides.

Pure Nafion NR50 polymer although more thermally stable than Amberlyst, has extremely low surface area (below 1 m^2/g) what limits its application. In methanolysis of triacetin no leaching of S-species was observed however its activity changed to swelling effect [7]. Nafion resin-based silica nanocomposites in which nanometer sized Nafion resin particles were entrapped within a highly porous silica network have much larger surface area, ca. 200 m^2/g [15,22]. As the result the catalytic activity of this nanocomposite material per unit mass of Nafion resin was found to be much higher compared to pure Nafion NR50 polymer because the majority of the acid sites were accessible to reagents [22]. The activity of Nafion SAC-13 composite was not reduced in successive cycle of triacetin methanolysis and esterification of palmitic acid [22,23].

By incorporation of organosulfonic groups into mesostructured silica SBA-15, a new type of solid acid catalysts of well defined porosity, high surface area and easily accessible active centres were obtained [24,25]. The activity of propylsulfonic acid-functionalized SBA-15 catalyst in esterification of free fatty acids present in beef tallow was comparable to that of Nafion NR50, however the catalysts deactivated due to the condensation of reagents in the mesopores of catalysts. This was explained by too high polarity of the catalyst. Bifunctionalization of the SBA-silica support via simultaneous incorporation of propylsulfonic groups and propyl groups resulted in enhanced hydrophobicity of the catalyst thereby diminishing the interaction of the polar molecules with the sulfonic acid groups, a reason of catalyst deactivation. Melero et al. [25] demonstrated very promising performance of propylsulfonic acid-modified SBA-15 catalyst towards simultaneous esterification of fatty acids and transesterification of triglycerides using refined and crude vegetable oils. Significant activity of these catalysts was attributed to the large surface area and pore diameter of the mesoporous support as well as the moderate acid strength. Caetano et al. [26] studied sulfonic acid-containing resin-based on poly(vinyl alcohol) (PVA), prepared by crosslinking the PVA with sulfosuccinic acid. Such resins displayed much better catalytic performance in term of activity and stability than commercial Nafion NR50 and Dowex resins in both esterification of palmitic acid and transesterification of soybean oil carried out in a membrane reactor [27].

In the present work, other polymeric catalyst, polyaniline-sulfate (PANI-S) is evaluated in transesterification of triglycerides and in esterification of fatty acid. The commonly used term “polyaniline” refers to a polymer (Scheme 2) prepared by the oxidative polymerization of aniline [28]. Due to basic character of nitrogen-containing groups (imine groups –N=, pK_a = 2.5, amine ones –NH–, pK_a = 5.5 [29]), polyaniline can be easily protonated at imine sites with protonic acids to give the “polyaniline-salt”, such as hydrochloride, nitrate, phosphate, sulfate etc. Polyaniline-salts are organic semiconductors. They are easy to prepare, handle, and they exhibit good environmental and thermal stability (up temp ca. 300 °C) and are insoluble in most of organic solvents. These properties make polyaniline-salts a potential candidate to be used



Scheme 2. Polyaniline-base and its two-step protonation with sulfuric acid to polyaniline-sulfate and subsequently to polyaniline-hydrogen sulfate.