Fuel 116 (2014) 760–771

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Organo-sulfonic acids doped polyaniline – based solid acid catalysts for the formation of bio-esters in transesterification and esterification reactions

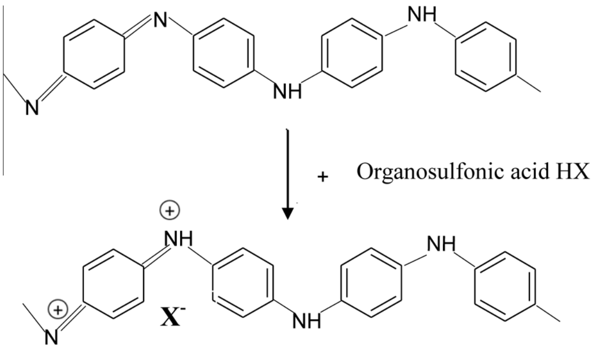
A. Drelinkiewicz *, Z. Kalemba-Jaje, E. Lalik, R. Kosydar

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Kraków, Poland

HIGHLIGHTS

- Transesterification of triacetin and castor oil with methanol.
- Esterification of ricinoleic acid with methanol.
- Organo-sulfonic acids doped polyaniline catalysts.
- A role of acid sites strength and capacity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 June 2013
Received in revised form 27 August 2013
Accepted 29 August 2013
Available online 10 September 2013

Keywords:
Biodiesel
Transesterification
Triacetin
Castor oil
Ricinoleic acid

ABSTRACT

In the present work catalytic reactivity of polyaniline protonated with organo-sulfonic acids, namely methanosulfonic (MSA-Pani), camphorosulfonic (CSA-Pani) and lignosulfonic (LG-Pani) acids was evaluated for the transesterification of triglycerides (triacetin, castor oil) and esterification of fatty acid (ricinoleic) with methanol. Their reactivity was also compared with previously studied alkyl-free polyaniline-sulfate (S-Pani) catalyst. The textural and acid properties of the catalysts before and after catalytic tests were characterized by BET, FT-IR, XRD, SEM, thermogravimetric and ammonia sorption techniques. It was observed that acid characteristics, namely concentration and the strength of acid sites as well as chemical properties of the surface e.g. the type of organo-sulfonic acid played an important role in catalytic performance of studied samples. In all tested reactions, the MSA- and CSA-doped polyanilines exhibited the highest initial activity referred to the acid site capacity. However, too weak acid sites in these catalysts resulted in their partial blockage during methanolysis of triglycerides. This was not observed in the esterification reaction. Among all studied samples, the LG-Pani (commercial reagent) and MSA-Pani catalysts seem to be the most promising owing to their high activity and good stability in reaction mixture, in particular during methanolysis of triglycerides. In contrast to the MSA-Pani catalyst (thermally stable up to 260 °C), lower stability of LG-Pani catalyst (up to ca. 120 °C) may limit its application.

1. Introduction

Biodiesel is a nonpetroleum-based fuel that consists of alkyl esters derived from the transesterification of triglycerides or the esterification of free fatty acids with short-chain alcohols (methanol). The conventional production process consists of the use of alkaline homogeneous catalyst, such as sodium hydroxide or sodium metoxide. However, they suffer from drawbacks, such as their corrosive nature and environmental pollutions. Moreover, they cannot be easily separated from the reaction mixture. Heterogeneous catalysts are an attractive alternative for several reasons

---

* Corresponding author. Tel.: +48 126395114.
E-mail address: ncdrelin@cyf-kr.edu.pl (A. Drelinkiewicz).

0016-2361/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2013.08.079

including: easy separation from product, greater tolerance of free fatty acid and water in feed-stocks, saponification side-reaction is eliminated. Heterogeneous acid catalysts have further substantial advantages as they are able to simultaneously catalyze transesterification of triglycerides and esterification of free fatty acids present in low grade oil feed stock.

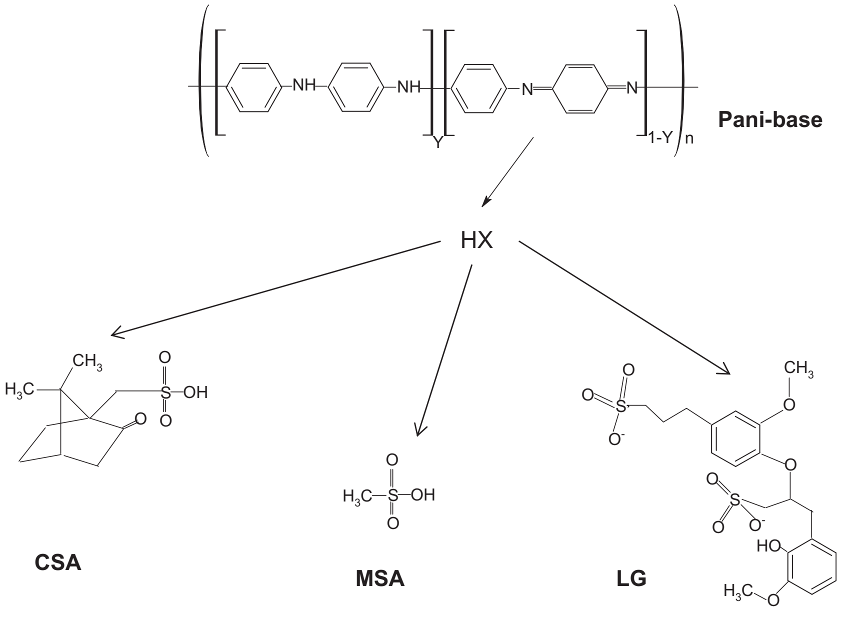
A variety of solid acids has already been tested [1–5] and the sulfonic acid-based catalysts have been found to be a promising candidates. They include sulphated metal oxides (zirconia, titania, tin oxide) as well as sulfonic groups attached to the polymer backbone, such as in Amberlyst-series, Nafion NR and Nafion SAC-13 composite [5–7], (Polystyrene–divinylbenzene)-based sulfonic acid [8], sulfonated poly(styrene-co-divinylbenzene) and sulfonated poly(divinylbenzene) [9] hypercrosslinked polystyrene [10], the “sugar catalysts” prepared by incomplete carbonization of simple carbohydrates (starch, cellulose, glucose, sucrose) followed by sulfonation [11,12], sulfonated amorphous carbon [13] and biochar-based catalysts [14].

In the literature there are numerous examples demonstrating high efficiency of hybrid materials obtained by functionalization of the mesoporous silica materials (MCM-41, SBA-2, SBA-15) with organo-sulfonic acids such as propylsulfonic, phenylsulphonic acids [15–21]. This modification altered chemical and textural features of silica. In particular it improved hydrophobicity near the active sites thus enhancing diffusion of reactants and products within the hydrophobic porous structure. Introduction of these hydrophobic groups also inhibited the poisoning of the acid sites due to water, a product of esterification reaction. As a result, these catalysts exhibited improved performance in terms of higher activity and lower deactivation observed either in esterification of free fatty acids or transesterification of mixture consisting of oils and fatty acids. The type of organosulfonic acid group anchored to the silica surface was observed to significantly affect their activity [15,22,23]. SBA-15 functionalized with benzenesulfonic acid exhibited much higher activity than propylsulfonic acid-modified sample [19,23–25]. This was explained by higher strength of the SO_3H sites in the phenyl groups-containing samples. An enhancement of the acid strength in the phenyl-SO_3H–SBA-15 relative to propylsulfonic SBA-15 catalysts was related by Melero et al. [26,27] to the presence of more electron withdrawing substituents in the molecular environment of the SO_3H sites. However, these silica-based catalysts were deactivated to some extent during the reactions because hydrophilic surface of silica facilitated sorption of water molecules (reaction product).

Further functionalization of these hybrid catalysts with organic groups (methyl, ethyl, propyl, phenyl) [18,19,21,27] enhanced their catalytic performance by surface hydrophobization due to capping the free surface Si—OH groups with an alkyl-based silanes. The type and the concentration of organic alkyl groups, the alkyl/sulfonic ratio as well as the location of the hydrophobic organic groups (outer surface/pore structure) all contributed to the performance of these catalysts [19]. An enhancement in their performance was also dependent on the type of fatty acid reactant in the esterification reaction. The size and the structure of fatty acid alkyl group played a role via steric effect [21]. Moreover, the presence of hydrophobic ethyl groups in the sulfonic acid-modified SBA-15 was reported to exhibit a positive effect on initial catalyst activity in the esterification of octanoic acid whereas did not affect the activity in transesterification of triacetin, a short triglyceride molecule [28]. In spite of a number of advantages observed for such ogranosulfonic acid/silica-based catalysts, some deactivation problems have also been encountered during their use [17,29].

In the present work various organo-sulfonic acids doped polymer, namely polyaniline is examined. The samples of polyaniline doped with methanosulfonic (MSA-Pani), camphorosulfonic (CSA-Pani) and lignosulfonic (LG-Pani) acids are studied (Scheme 1). Polyanilines doped with various acids, such as p-toluenesulfonic, H_2SO_4, HCl, HNO_3, have already been explored by Palaniappan et al. [30,31] for various organic transformations, among them for the esterification of carboxylic acids with alcohols, transesterification of ketoesters. The activity of these polyaniline-salts varied depending on the type of doping acid and p-toluenesulfonic doped polymer was the most active catalyst. The polyaniline salts exhibited high stability resulting in good reusability in studied reactions.

Here, catalytic properties of the samples are evaluated in the transesterification of triglycerides and esterification of fatty acid with methanol. The triglyceride reactants are a short molecule of triacetin and bulky triglycerides of castor oil. The esterification reaction is studied for ricinoleic acid. Catalytic performance of these organo-sulfonic group-containing catalysts is compared with



Scheme 1. Schematic presentation of protonation of polyaniline base with acids; methanosulfonic (MSA), camphorosulfonic (CSA) and lignosulfonic (LG).