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Transesterification of triacetin with methanol on Nafion® acid resins

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Abstract

Although homogeneous alkali catalysts (e.g., NaOH) are commonly used to produce biodiesel by transesterification of triglycerides (vegetable oils and animal fats) and methanol, solid acid catalysts, such as acidic resins, are attractive alternatives because they are easy to separate and recover from the product mixture and also show significant activity in the presence of fatty acid impurities, which are common in low-cost feedstocks. To better understand solid acid catalyst performance, a fundamental transesterification kinetic study was carried out using triacetin and methanol on Nafion® (perfluorinated-based ion-exchange resin) catalysts. In particular, Nafion® SAC-13 (silica-supported Nafion) and Nafion® NR50 (unsupported Nafion) were investigated, because both show great promise for biodiesel-forming reactions. The reaction kinetics for a common homogeneous acid catalyst (H_2SO_4) were also determined for comparison. Liquid-phase reaction was performed at 60 °C using a stirred batch reactor. The swelling properties of the resin in solvents of diverse polarity that reflect solutions typically present in a biodiesel synthesis mixture were examined. The initial reaction rate was greatly affected by the extent of swelling of the resin, where, as expected, a greater effect was observed for Nafion® NR50 than for the highly dispersed Nafion® SAC-13. The reaction orders for triacetin and methanol on Nafion® SAC-13 were 0.90 and 0.88, respectively, similar to the reaction orders determined for H_2SO_4 (1.02 and 1.00, respectively). The apparent activation energy for the conversion of triacetin to diacetin was 48.5 kJ/mol for Nafion® SAC-13, comparable to that for H_2SO_4 (46.1 kJ/mol). Selective poisoning of the Brønsted acid sites on Nafion® SAC-13 using pyridine before transesterification revealed that only one site was involved in the rate-limiting step. These results suggest that reaction catalyzed by the ion-exchange resin can be considered to follow a mechanism similar to that of the homogeneous catalyzed one, where protonated triglyceride (on the catalyst surface) reaction with methanol is the rate-limiting step.

Keywords: Biodiesel; Triacetin; Methanol; Transesterification; Sulfonic acid resins; Nafion® SAC-13; Nafion® NR50; Polymer swelling; H_2SO_4

1. Introduction

Recent concerns about the increasing cost of petroleum-derived fuels have excited interest in the production of renewable fuels, especially biodiesel. Biodiesel consists of fatty acid alkyl esters that are commonly derived from vegetable oils. Conversion of these oils, consisting primarily of triglycerides, to biodiesel fuel is commonly achieved through a series of transesterification reactions involving the reaction of an alkoxy group of an ester (i.e., mono-, di-, or triglyceride) with that of a small alcohol (e.g., methanol or ethanol). This reaction has traditionally been catalyzed by homogeneous catalysts, such as alkaline bases or mineral acids [1–6]. However, environmental and economic concerns are such that a continuous process that uses a heterogeneous catalyst is much more desirable. In particular, solid acid catalysts are ideal because they are able to catalyze both transesterification and esterification reactions simultaneously, which becomes important when using lower-quality feedstocks (e.g., used deep-frying oils) [7–9].

Sulfonic resins compose a group of acid catalysts that can be classified according to the polymer backbone, namely polystyrene (e.g., Amberlyst® resins) or perfluorinated alkanes (e.g., Nafion® resins) [10]. These acid resins have inherently low surface areas unless a solvent is used to swell the polymer, thereby exposing additional internal acid sites for reaction. Because high surface areas are more desirable for heterogeneous catalysis, increased polymer surface area (without relying on solvent swelling) can be achieved by supporting these polymers on inert high-surface area oxide materials. For example, Nafion® SAC-13 is a highly acidic Nafion®–

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Table 1
Physicochemical characteristics of Nafion® SAC-13 and Nafion® NR50

Parameter	Nafion® SAC-13	Nafion® NR50
Support	SiO_2	None
Composition	Fluorosulfonic acid Nafion® polymer (10–20 wt%) on amorphous silica (porous nanocomposite)[a]	Fluorosulfonic acid Nafion® polymer
Acidic group	$–CF_2CF_2SO_3H$	$–CF_2CF_2SO_3H$
Ionic form	H^+	H^+
Exchange capacity	150 μeq/g[b] (120–1000 μeq/g)[a]	⩾800 μeq/g[a] (>90%)[b]
Pellet shape	Lobular, lengthwise striations	Cylindrical and spherical
Pellet size	+20 mesh (diameter ∼1 mm, length/diameter = 9.4)[c]	7–9 mesh (1.6–2.8 mm)[d]
Pore volume	>0.6 mL/g[a]	N/A
Pore diameter	>10 nm[a]	N/A
Bulk density	0.4–0.5 g/mL[a]	N/A
Polymer density	2.1 g/mL[a]	2.1 g/mL[a]
Surface area	>200 m^2/g[a]	–

[a] General information provided by the manufacturer.
[b] Specific information provided by the manufacturer for the Nafion® NR50 utilized (batch # 04601MB).
[c] Specific information provided by the manufacturer for the Nafion® SAC-13 utilized (batch # 05729PC).
[d] Catalyst not swelled.

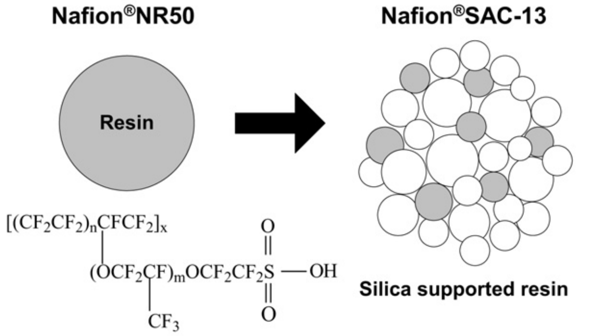

Fig. 1. Schematic of the Nafion® catalysts: $m = 1$, 2 or 3, $n = 6–7$, and $x \sim 1000$. Redrawn from Ref. [11].

silica nanocomposite (Fig. 1) that contains 13 wt% Nafion, which is a copolymer of tetrafluoroethylene and perfluoro-2-(fluorosulfonylethoxy)propyl vinyl ether. The small (5–30 nm) Nafion® resin particles [11] are entrapped within the porous silica matrix. This acid catalyst has been shown to effectively catalyze numerous industrial reactions, including olefin isomerizations, alkylations, acylations, oligomerizations, esterifications, and others [11–13]. A more detailed list of the physicochemical properties of this type of catalyst is provided in Table 1.

Although the use of solid acid catalysts for the continuous production of biodiesel is promising, only limited information exists about triglyceride transesterification rates or the extent of catalyst deactivation [7,14–18]. We previously reported, based on turnover frequency (TOF) results, that solid acid catalysts, such as Nafion® NR50, sulphated zirconia (SZ), and tungstated zirconia (WZ), have sufficient acid site strength to catalyze biodiesel-forming transesterification reactions as efficiently as sulfuric acid [15]. In the same study, Nafion® NR50 was found to give higher selectivity to final products (methyl ester and glycerol) compared with other solid acid catalysts. Because of the significant acid strength and selectivity of Nafion® NR50 and improved surface area of Nafion® SAC-13 (without relying on solvent swelling), these catalysts were chosen for more detailed kinetic and mechanistic studies of the liquid-phase transesterification of triacetin ($C_9H_{14}O_6$) and methanol. Reaction catalyzed by sulfuric acid was also studied for comparison. All three catalysts have only Brønsted acid sites. The consecutive transesterification reactions occurring in the conversion of triacetin to diglycerides, monoglycerides, glycerol, and esters have been illustrated elsewhere [15]. Triacetin was used as a model triglyceride for the detailed kinetic study because it can be obtained in a pure form and has all carboxylic side groups identical (acetic acid), thereby facilitating the kinetic analysis of reaction. Although there is a decrease in reaction rate as the carboxylic acid side groups grow larger, preliminary results have shown that the reaction rates of small triglycerides are directly related to those of much larger triglycerides.

2. Experimental

2.1. Materials

Nafion® SAC-13, Nafion® NR50, triacetin (99.5 wt%), methanol (99.9 wt%), acetic acid (99.7 wt%), tetrahydrofuran (99.9 wt%), pyridine (99+ wt%), methyl acetate (99 wt%), acetins mixture (45 wt% diacetin, 26 wt% monoacetin, 25 wt% triacetin, and 4 wt% glycerol), and refined olive oil (low acidity) were purchased from Sigma-Aldrich and used as received. Ethanol solvent (99.5 wt%), toluene (99.8 wt%) internal standard, and H_2SO_4 (95–98 wt%) were obtained from Acros Organics, Fisher Scientific, and EMD, respectively.

2.2. Catalyst characterization

So as to be able to relate the observed kinetic behavior with catalyst properties, several analytical techniques were used to probe relevant physicochemical properties of the Nafion® SAC-13 and Nafion® NR50 catalysts studied. Catalyst total surface area (S_{BET}) was determined by BET analysis as described previously [15]. Analogous conditions were used here to determine pore volume and average pore size in a Micromeritics ASAP 2020 instrument.