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Esterification and transesterification on tungstated zirconia: Effect of calcination temperature

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Abstract

As part of ongoing efforts to investigate heterogeneous catalysts for biodiesel synthesis, the catalytic activity of the strong solid acid tungstated zirconia (WZ) was studied for the esterification of acetic acid (in both the gas and liquid phase) and the transesterification of triacetin (a synthetic triglyceride in the liquid phase) with methanol. Acetic acid and triacetin were used as model compounds for free fatty acids (FFAs) and triglycerides, respectively. Complex mixtures of FFAs and triglycerides are typical biodiesel precursors found in unrefined vegetable oils, animal fats, and waste greases. The effect of calcination temperature (400–900 °C) on the catalytic properties of WZ was investigated with the goal of determining the optimum pretreatment temperature and increasing the understanding of the nature of the active sites for esterification and transesterification. Catalyst characterization by powder X-ray diffraction, Raman spectroscopy, TGA, elemental analysis, and total BET surface area allowed us to correlate the changes in catalyst physicochemical properties with calcination temperature. Ion-exchange/titration and NH_3-TPD were used to characterize the number and strength of the acid sites. Esterification and transesterification rates (on a catalyst weight basis) increased with increasing surface WO_x densities between 1.9 and 6.6 W-atoms nm^{-2} and then decreased for densities above 6.6 W-atoms nm^{-2}. The growth of WO_3 crystalline species resulted in lower esterification and transesterification rates, consistent with a decrease in the number of active sites. For the catalyst that exhibited the optimum catalytic activity (calcined at 800 °C), selective poisoning of the potential catalytic centers revealed that Brønsted sites play the major role in carrying out these reactions.

Keywords: Acetic acid; Triacetin; Esterification; Transesterification; Tungstated zirconia; WZ; Calcination effect; Selective poisoning; Brønsted versus Lewis acidity; Sites

1. Introduction

Environmental and economic considerations have made the production of renewable resource fuels highly advantageous. Biodiesel has received particular attention because it can be prepared from a variety of vegetable oils and animal fats and is readily used in existing diesel engines. Biodiesel production costs could be further improved if lower cost feedstocks, such as used cooking oils and animal fats, could be easily converted. These feedstocks often contain significant quantities of free fatty acids (FFAs) and water, which make them unsuitable for existing homogeneous alkaline-catalyzed processes. Neutralization of FFAs can be carried out by the addition of excess alkali, but this leads to the formation of soaps and to post-reaction separation problems. Thus, a preferred pretreatment process for used cooking oils is an esterification process that commonly uses a strong liquid acid catalyst, such as sulfuric acid [1–5]. However, the use of this strong acid mandates the use of costly corrosion-resistant materials and neutralization of the reaction mixture after esterification before the subsequent homogeneous base-catalyzed transesterification.

The use of solid acid catalysts offers many advantages over existing homogeneous catalysts used in biodiesel synthesis [6]. For example, solid acid catalysts have the ability to simultaneously catalyze transesterification and esterification reactions. Among strong solid acid catalysts, sulfated zirconia (SZ) and Nafion resin catalysts have been shown to catalyze biodiesel forming reactions as efficiently as sulfuric acid on a site activity basis [7,8]. Nevertheless, SZ is known to suffer significant

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deactivation during liquid-phase transesterification [7,9], possibly due to sulfur leaching at even mild temperatures (60 °C). Nafion resins (e.g., NafionSAC-13 and NafionNR50), on the other hand, are effective in esterification and transesterification reactions [7,8,10–12] and tend to maintain higher catalytic activities, especially when the water byproduct is stripped off during reaction [12]. However, to preserve resin stability, the temperature of operation must be kept below 280 °C [8], and there is evidence that larger reactant molecules lead to greater deactivation, perhaps due to entanglement with the catalyst polymeric chains [11].

Supported tungsten oxide catalysts have recently received much attention because of their acid properties and their ability to catalyze both esterification and transesterification reactions, which play major roles in biodiesel production [7,13–15]. Furuta et al. [13] reported that soybean oil can be efficiently converted to methyl esters at a reaction temperature of 250 °C using tungstated zirconia alumina (WZA) calcined at 800 °C. The addition of Al_2O_3 further stabilizes the tetragonal phase of the ZrO_2 support and also prevents the growth of WO_3 particles [16]. WZA is also suitable for the esterification of *n*-octanoic acid, showing promise for application in biodiesel synthesis from lower-quality feedstocks. Another study that investigated the esterification of palmitic acid with methanol on WZ found correlations among the conversion of palmitic acid, the acidity of WZ (as measured by NH_3-TPD), and the percentage of tetragonal phase of the ZrO_2 support [14]. More recently, we have reported, based on turnover frequency (TOF) results, that WZ has a site activity comparable to H_2SO_4 for catalyzing biodiesel-forming transesterification reactions [7]. Another advantage of WZ is that catalyst deactivation appears to be not rapid for transesterification of triglycerides with methanol [7,13].

Earlier studies have used this strong acid catalyst for a variety of reactions, including alkane isomerization [17–21] and alcohol dehydration [22,23]. More fundamental studies of WZ have also examined how the nature of the active sites influences the observed catalytic activity of the material [24–35]. Hino and Arata [17,18] first reported the formation of so-called "superacid" sites ($H_0 = -14.52$) on WZ (13 wt% W) for isomerization of butane and pentane, as well as Friedel–Craft acylations as a function of preparation conditions and calcination temperatures. These authors found that heating a combination of tungsten species and zirconium oxide to temperatures that would create a tetragonal zirconia phase led to the formation of catalysts with higher activity. Since then, many investigations have attempted to characterize the active sites formed on WZ catalysts [24–35]. Iglesia and coworkers have extensively studied the structural changes of WZ with calcination and tungsten loading [20,22,23,31,33,36]. These authors showed that turnover rates (for xylene isomerization and alcohol dehydration) were solely a function of the tungsten surface density, which changes with tungsten loading and calcination temperature. Despite the great amount of literature dealing with WZ surface catalytic properties, agreement on what constitutes the most active sites has not yet been reached. However, it has been observed that the formation of surface polymeric tungsten species correlates well with increases in WZ catalyst activity [31].

The transesterification of triglycerides using acid catalysts has been little studied. A major objective of the present study was to increase the understanding of the catalytic activity of strong solid acids (WZ) for biodiesel-forming type reactions. Esterification of acetic acid (gas and liquid phase) and transesterification of triacetin (liquid phase) with methanol were used as probe reactions. Triacetin is a synthetic triglyceride-like molecule that has the shortest possible alkyl chain length (a single $-CH_3$ moiety on each branch). Of particular interest was the effect of calcination temperature on WZ catalytic activity for the transesterification of triglycerides, because, to the best of our knowledge, no previous publication has addressed this issue.

2. Experimental

2.1. Materials

Triacetin (99.5 wt%), methanol (99.9 wt%), acetic acid (99.7 wt%), methyl acetate (99 wt%), an acetin mixture (45 wt% diacetin, 26 wt% monoacetin, 25 wt% triacetin, and 4 wt% glycerol), pyridine (99.9%), and di-*tert*-butyl-pyridine (97%) were purchased from Sigma–Aldrich and used as received. For GC analysis, ethanol (99.5 wt%; Acros Organics) was used as a solvent and toluene (99.8 wt%; Fisher Scientific) was used as the internal standard. Amorphous tungstated zirconia hydroxide precursor, XZO1251 (16 wt% WO_3), was provided by Magnesium Electron, Inc. (MEI, Manchester, UK). To activate the catalyst, WZ precursor samples were dehydrated at 120 °C for 1 h and then pretreated for 3 h under an air (zero grade) atmosphere in a furnace at calcination temperatures between 400 and 900 °C.

2.2. Catalyst characterization

Elemental analysis for tungsten was performed using inductively coupled plasma emission spectroscopy (Galbraith Laboratory, Knoxville, TN). Catalyst samples were calcined at 700, 800, or 900 °C before shipping to the external laboratory for elemental analysis. Catalyst total surface area (S_{BET}) was determined using a multipoint BET method. Before S_{BET} analysis, the catalyst samples were degassed at 200 °C and 10^{-3} Torr for 3 h. Adsorption measurements were carried out using UHP N_2 at –196 °C in a Micromeritics ASAP 2020 device. Catalyst thermal stability and degradation behavior were determined by thermogravimetric analysis using a Perkin–Elmer Pyris 1 TGA. Sample weight changes were recorded as an amorphous WZ precursor sample (8 mg) was heated at a rate of 20 °C/min from room temperature to 1000 °C under an atmosphere of air (zero grade), similar to the catalyst calcination conditions. NH_3-TPD was used to determine the acid site concentration and strength distribution of the WZ samples, as described previously [7]. The number of acid sites was also estimated by using a method involving an aqueous ion-exchange step of the catalyst H^+