Triglyceride Transesterification using Solid Base Catalysts

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Introduction

Triglyceride (TG) transesterification with low molecular weight alcohols such as methanol and ethanol is the main reaction for the synthesis of biodiesel (the term biodiesel currently designates mixtures of monoalkyl esters of fatty acids used as fuel [1, 2]). Nowadays, most commercial applications of TG transesterification for biodiesel synthesis use homogenous base catalysts like NaOH, KOH and MeONa. The use of this type of catalysts has many drawbacks, such as high corrosiveness, the need for intensive biodiesel separation and purification protocols, and the impossibility for catalyst reuse. Many authors have proposed solid catalysts to replace homogenous ones. So far, however, even though several studies have addressed the use of solid catalysts for biodiesel synthesis, the fact remains that only a handful of reports show meaningful discussions regarding how solid catalysts operate from a chemical standpoint and what the most important variables are for their successful use. In addition, the literature is lacking in studies on catalyst re-usability and regeneration, key issues for commercial application.

This presentation will show some of our results on the use of solid bases for TG transesterification using both model compounds for TGs and real TG feedstocks. Solid bases with different types of active sites, i.e., with Lewis base sites vs. Brønsted base sites, have been studied and their catalytic activities examined in terms of their chemical properties and the nature of the active sites carrying out catalysis. Conclusions about the potential practical application of these materials have been drawn from re-usability and regeneration studies.

Materials and Methods

Anhydrous reagents were used without further purification. High grade poultry fat with an acid content of less than 0.2% and a water content of 0.05% was kindly provided by Fieldale Farms Corporation. Appropriate standards and methods were used for GC calibration and analysis. The polystyrene based resin with tetramethyl ammonium hydroxide groups, A26, and the silica based materials, 3-(trimethylammonium)-propyl-functionalized silica gel chloride form (QN^+Cl^-/SiO_2), as well as a commercially available hydrotalcite, $Mg_6Al_2(CO_3)(OH)_{16}\cdot 4H_2O$, were purchased from Aldrich. Prior to reaction, A26 was thoroughly washed with methanol and then dried under vacuum. QN^+Cl^-/SiO_2 was converted into QN^+OH^-/SiO_2 using a $N(Me)_4OH$ methanolic solution. The solid was recovered by filtration and then extensively washed with methanol at room temperature. Catalyst samples were characterized by elemental analysis (Galbraith Lab., Knoxville, TN) and isothermal N_2 adsorption (Micromeritics ASAP 2002). Reaction experiments were carried out in isothermal well-stirred batch reactors under a nitrogen atmosphere. A Hewlett-Packard 6890 gas chromatograph equipped with a DB-1 column was used for sample analysis.

Results and Discussion

The transesterification of TG model compounds with methanol was successfully carried out under mild reaction conditions using solid catalysts with Brønsted base functionality of organic ammonium quaternary ions bonded to either silica or an organic polymeric matrix. The support played an important role in catalyst selectivity and deactivation behavior. Despite a greater site activity, the basic groups grafted to silica were less selective for glycerol and more prone to deactivation. The polymeric resin catalyst, on the other hand, exhibited outstanding features, such as great capacity to drive the series reaction of glycerides to completion and to sustain high activity through multiple reaction cycles without signs of significant deactivation. This catalyst appears as an interesting alternative to strong soluble inorganic bases for TG transesterication. Thermal stability and the capacity to catalyze the transesterification of large TG compounds, however, are at issue with this catalyst.

The use of heterogeneous base catalysts with only Lewis base site functionality derived from a Mg-Al hydrotalcite, on the other hand, showed high activity for the transesterification of large TGs at moderate temperatures (120°C) without sign of catalyst leaching. Leaching of active sites has been a concern for other solid bases working through strong Lewis base sites [3]. Catalytic performance was significantly affected by pretreatment and operating conditions. Calcination at 550°C gave rise to the most active material. Rehydration of the calcined catalyst before reaction, however, decreased catalytic activity. Pre-contact of the catalyst with the TG feedstock (poultry fat) resulted in diminished catalyst activity. Most likely, catalyst deactivation took place due to the strong adsorption (potentially irreversible) of the heavy lipid compounds on the catalyst surface as model compound studies have suggested. The catalyst underwent significant deactivation during the first reaction cycle probably due to deactivation of the strongest most accessible base sites. Nevertheless, a simple re-calcination resulted in almost complete restoration of catalyst activity.

Significance

The use of heterogeneous rather than homogenous catalysts for biodiesel synthesis should impact the cost of producing biodiesel, providing a more environmentally benign way to obtain a biofuel that lowers our dependence of foreign oil and strengthens our economy.

References

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