Assessing the activity of heteropolyacid tin salts catalysts in the oleic acid esterification reactions to produce biodiesel

Marcio J. da Silva (PQ)*[1]; Thalhyta M. S. Santos (IC)[1], Suzane M. da Silva (IC)[1]

[1]*Universidade Federal de Viçosa, Avenida P.H. Rolfs, s/n, Viçosa, Minas Gerais, Brasil, CEP 36570-000.*

Keywords: *Heteropolyacids, biodiesel, zinc catalysts, esterification reactions, free fatty acids.*

Introduction

Free fatty acids are present in high concentration in non-edible oils and animal fats, which are inexpensive feedstock to make biodiesel. Homogeneous mineral acids efficiently catalyzes these reactions, however, they generate large amount of effluents and neutralization residues [1]. Therefore, to develop active and reusable catalysts to produce biodiesel through friendly environmentally processes is a challenge to be overcomes. On this regard, heteropolyacids (HPAs) are still an attractive alternative that deserves be explored [2]. Keggin series HPAs are active catalysts used in reactions either in homogeneous or heterogeneous conditions. In this work, HPAs tin salts catalysts were prepared, characterized and evaluated on oleic acid esterification reactions with ethanol. The influence of Sn^{2+} cations and heteropolyanions as well as optimization of reaction conditions were investigated.

Results and Discussion

The synthesis of HPAs tin salts was performed by addition drop by drop of the HPA solution to the alcoholic solution of $SnCl_2$ salt. The solvent vaporization followed by the drying to 333 K during 8 hours gave a solid salt with a stoichiometric yielding. The characterization was carried out using FT-IR spectroscopy, which proved that Keggin anion remained untouchable. Thermal analyzes and AAS analyzes confirmed the presence of heteropolyacid crystallization water and tin content, respectively. The esterification reaction is a reversible acid-catalyzed process where an alcohol shifts equilibrium toward higher ester formation (Fig.1).

$$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$$

Figure 1. Acid-catalyzed esterification reactions.

Firstly, we assessed the precursors activity in the reactions carried out under homogeneous phase (Fig. 2). It was find out that after 8 hours reaction, high conversion of oleic acid to ethyl oleate has obtained regardless heteropolyacid employed. Although different acid nature, $SnCl_2$ achieved a conversion of 92 %. Although C_2H_5OH excess (*ca.* 16:1), a poor conversion was reached in the catalyst-free reaction.

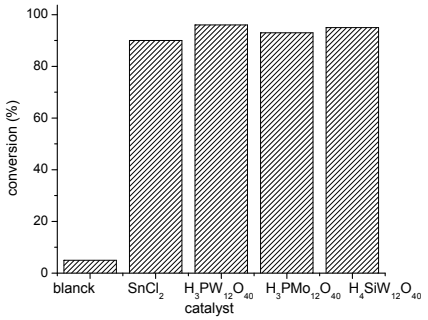

Figure 2. Acid-catalyzed oleic acid esterification

Although only partially soluble, HPAs tin salts were similarly active (Table 1).

Table 1. Oleic acid esterification reactions in presence of Sn-HPAs salts catalysts[a]

Run	Catalyst	Conversion (%)	Ester selectivity (%)
1	$Sn_3(PW_{12}O_{40})_2$	93	97
2	$Sn_3(PMo_{12}O_{40})_2$	90	96
3	$Sn_4(SiW_{12}O_{40})_2$	85	94

[a]Reaction conditions: magnetic stir, 333 K Temperature, FA: C_2H_5OH molar ratio equal 1:16, catalyst (10 mol %); 8 hours.

Conclusion

Although highly active, HPAs salt catalysts were partially soluble. It is suggestive that an adequate thermal treatment may make they totally insoluble and even active catalysts.

Acknowledgement

The authors thanks CNPq, FAPEMIG and CAPES.

[1] Da Silva, M. J.; Fernandes, S. A..; Cardoso, A. L. *Fuel Process. Technol.* **2012**, *96*, 98.
[2] Da Silva,; Cardoso, A. L.; Neves, S. C. G. *Energ Fuel,.* **2009**, *23*, 1718.