



Selective partial biodiesel hydrogenation using highly active supported palladium nanoparticles in imidazolium-based ionic liquid

Bruno S. Souza^a, David M.M. Pinho^b, Elder C. Leopoldino^a, Paulo A.Z. Suarez^{b,*}, Faruk Nome^{a,*}

^a Departamento de Química, Universidade Federal de Santa Catarina, SC 88040-900 Florianópolis, Brazil

^b Laboratório de Materiais e Combustíveis, Instituto de Química, Universidade de Brasília, Brasília, Brazil

ARTICLE INFO

Article history:

Received 15 February 2012

Received in revised form 8 May 2012

Accepted 9 May 2012

Available online 17 May 2012

Keywords:

Biodiesel

FAME

Palladium

Nanoparticles

Hydrogenation

Ionic liquid

ABSTRACT

The low oxidative stability of biodiesel derived from polyunsaturated oils is one of the great challenges to be overcome in biodiesel technology. Here, we use a high activity catalyst Pd/ImS3-12@Al₂O₃, prepared by adsorption of water-prepared palladium nanoparticles on aluminum oxide, for partial biodiesel hydrogenation. The catalyst shows higher hydrogenation activity than conventional Pd/C, leading in the absence of ionic liquid (IL) to fully hydrogenated product. In the presence of BMIM-NTf₂ (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) IL the activity of the Pd/ImS3-12@Al₂O₃ catalyst could be controlled and selective reduction to monoene product, with large preference for formation of the *cis* isomer, could be achieved at low temperature and pressure, with very low catalyst loading, no detectable metal leaching and good recyclability. The partially hydrogenated biodiesel is far more stable to oxidation than the crude, without compromising its cold-flow properties.

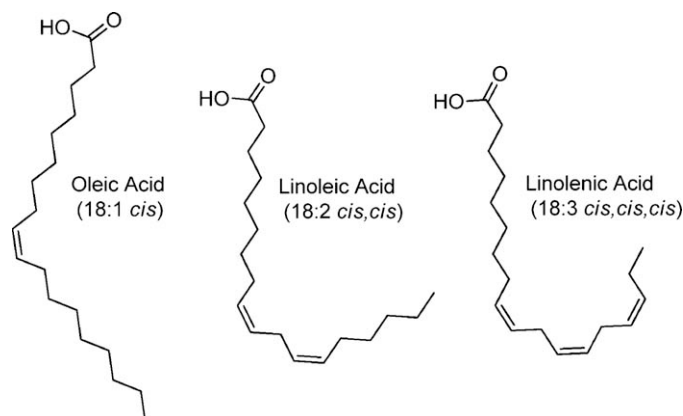
© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Biodiesel derived from polyunsaturated oils, such as soybean oil, is the alternative of choice for countries like Brazil and US. However, the high degree of polyunsaturated fatty acids in soy bean oil, mainly linoleic (two double bonds, *ca.* 58%) and linolenic (three double bonds, 6%), [Scheme 1](#), leads to several issues concerning oxidative and thermal stability [\[1\]](#). One approach to address this issue is hydrogenation [\[2\]](#). However, complete catalytic hydrogenation to saturated chains dramatically increases the melting point of biodiesel, compromising its cold flow properties [\[3\]](#). This problem could be solved with a catalytic system that allows a partial and selective hydrogenation leading to mainly oleic (18 carbons with one *cis* double bond) chain formation. Another drawback commonly observed on hydrogenating partially polyunsaturated olefins is the conversion of *cis*- into the more thermodynamically favored *trans*-double bonds. In the case of biodiesel, the side isomerization of oleic into elaidic chains (18 carbons with one *trans* double bond) is particularly undesirable due to the lower crystallization point of the *trans* isomers when compared with those of *cis* [\[4\]](#), which also compromises the cold flow properties of the fuel.

Among the various metals studied in nanocatalysis, palladium has received great attention due to its wide applicability, such as

alkene hydrogenation [\[5\]](#), C–C coupling reactions [\[6\]](#) and reduction of aromatic nitro compounds [\[7\]](#). Since the oxidative stability depends on the degree of unsaturation of the soybean fatty acid methyl esters (FAMES) chain, we are particularly interested in the selective hydrogenation of polyolefins. Indeed, avoiding complete hydrogenation and *cis/trans* isomerization is a major challenge in hydrogenation. Some of us have recently used the hydrogenation of FAME as a probe to study the selectivity of palladium nanoparticles in hydrogenation [\[2\]](#). It was observed that 4–6 nm palladium



Scheme 1. Main fatty acids present as glycerol esters in soybean oil.

* Corresponding authors. Tel.: +55 048 37216849; fax: +55 048 37216850.

E-mail address: faruk.nome@ufsc.br (F. Nome).