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Research paper

Palladium supported on clays to catalytic deoxygenation of soybean fatty acids

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ABSTRACT

This work aims at the soybean free fatty acid deoxygenation using palladium supported (1 wt.%) on different clays as catalysts. The results presented a promising technology for the single-stage production of hydrocarbons in the diesel fuel range. Clays used as palladium support were a natural Brazilian Montmorillonite (BM), this same clay in its pillared form (PILCBM) and two commercial clays (K10 and KSF). Catalysts were characterized by N_2 adsorption, X-ray diffraction (XRD), FTIR spectra of adsorbed pyridine, CO chemisorption and scanning electron microscopy (SEM). Reactions were carried out in batch mode, under different H_2 pressures (10, 20, 30 and 40 bar) at 300 °C. Reactions performed using Pd/K10 as catalyst at 30 bar of H_2 presented interesting results: 74.5% conversion after 6 h and selectivities to *n*- and *i*-alkanes equal to 69% and 29%, respectively.

1. Introduction

The large increase in energy consumption in the recent decades and the growing environmental awareness have turned renewable fuels to be an attractive alternative (Ping et al., 2011). Considerable efforts have been made to develop clean and renewable fuel technologies in order to secure the world energy reserves and gain environmental benefits (Lestari et al., 2009). Although biodiesel is a well-established additive to mineral diesel fuel, its use is associated with a number of specific problems. Consequently, there is a need to develop new and improved methods for producing motor fuels from natural raw materials (Kikhtyanin et al., 2010). A technology for converting free fatty acids in hydrocarbons in the diesel range, based on the deoxygenation reaction, has been recently developed (Kubičková et al., 2005; Mäki-Arvela et al., 2007, 2008; Rozmyszowicz et al., 2012; Snåre et al., 2006, 2007). However, despite the fact that *n*-paraffinic compounds are ideal components for the mixture with petroleum diesel, due to its high cetane number and environmental benefits, long chain alkanes present relatively high melting points, affecting negatively the flow properties of the fuel. In this way, catalytic reactions that could produce diesel fuel with good flow properties without additives and in a single stage reaction become interesting from economic and environmental point of view. Bifunctional metal-containing catalysts could be an interesting option, since these materials possess both metal active sites, which are responsible for deoxygenating free fatty acids, and acid sites that may perform the subsequent conversion of the obtained *n*-alkanes into *i*-alkanes.

Clay minerals are among the world's most important and useful industrial materials. Catalysts based on clays have been used in a wide variety of chemical reactions for many years. Natural untreated clays have a very low ability to catalyze reactions in either polar or nonpolar media. However, the structural properties of these materials can be modified by various activation methods in order to produce catalysts with high acidity, surface area, porosity, and thermal stability (Moronta et al., 2005). These materials are relatively inexpensive and may be produced on large scales primarily because the basic ingredient used in production is readily available from natural sources (Paiva et al., 2008). These reasons demonstrate the immense potential of the clay materials in catalysis. According to the exposed, four different clays were used as support for palladium catalysts, which were tested in free fatty acid deoxygenation, in a solvent free system and using as feedstock a mixture of free fatty acids obtained from non-catalytic hydrolysis of the degummed soybean oil. Results presented in this work are promising since they enable the use of acidic clay materials as catalysts to produce high quality renewable diesel fuel.

2. Experimental

2.1. Catalyst preparation

The four different clays used as support for palladium catalysts were: a natural Brazilian Montmorillonite (BM), this same clay pillared (PILCBM) and two acidic commercial clays (KSF and K10).

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