



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 N₂ 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 H₂ pressures (10, 20, 30 and 40 bar) at 300 °C. Reactions performed using Pd/K10 as catalyst at 30 bar of H₂ presented interesting results: 74.5% conversion after 6 h and selectivities to *n*- and *i*-alkanes equal to 69% and 29%, respectively.

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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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2.1.1. Pillared clay preparation

As mentioned previously, the starting material used to prepare the pillared clay was a Brazilian Montmorillonite (BM). The Al-PILCBM was synthesized by intercalating the polyoxocations prepared in a pillaring solution into the interlamellar space of the raw montmorillonite. This pillaring solution was prepared by slow addition of a $0.6 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution to another $0.6 \text{ mol} \cdot \text{L}^{-1}$ AlCl_3 solution under constant stirring for 2 h. Then, the oligomeric solution prepared was aged for 6 days at room temperature. Finally, the aged solution was slowly added to a suspension of BM in deionized water. The exchange process was carried out at room temperature for 2 h under constant stirring. The resulting Al-PILCBM was separated by filtration and washed with deionized water until $\text{pH} = 7$. The solid obtained was dried at 80°C for 12 h and calcined for 30 min at 150°C and 3 h at 450°C . This pillaring process followed the methodology described by [Pergher and Sprung \(2005\)](#).

2.1.2. Palladium impregnation

Palladium was introduced in the clays by incipient wetness impregnation, as described by [Cañizares et al. \(1998\)](#). A specific quantity of palladium(II) acetate – $\text{Pd}(\text{OAc})_2$ – solution in toluene was added to a pretreated support (450°C for 6 h – $2.5^\circ\text{C} \cdot \text{min}^{-1}$). The quantity used, equal to the pore volume of the support, was calculated to provide approximately 1 wt.% of palladium. The solvent was removed by evaporation. The samples were dried at 100°C for 12 h, and treated at 450°C ($2.5^\circ\text{C} \cdot \text{min}^{-1}$) for 6 h.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded in a Rigaku Miniflex II Diffractometer with a monochromator, using $\text{CuK}\alpha$ radiation (40 kV and 40 mA) in the range $3 < 2\theta < 90^\circ$. The stepsize was 0.05° with 2 s by step.

Textural characteristics, such as BET specific surface area, pore volume and average pore diameter (BJH method) were determined by N_2 adsorption–desorption at -196°C in a Micromeritics Tristar 3000. Prior to the analysis, samples were outgassed for 24 h at 200°C to eliminate the physically adsorbed moisture.

Chemical composition of the materials was determined by X-ray fluorescence (XRF) using a Bruker spectrometer (AXS S4 Explorer). SEM analyses were performed in a MEV – FEI Quanta 200 operating at 20 kV.

The clay acidity was determined by the pyridine adsorption–desorption method, monitored by FT-IR spectroscopy (Spectrum 100 FT-IR Spectrometer). A thin wafer of the pure sample (around 30 mg) was placed in a quartz infrared cell for in situ pyridine adsorption and desorption experiments. The wafer was heated under vacuum (10^{-4} Torr) at 450°C for 1 h and, after cooling to room temperature, an FTIR spectrum of the vacuum treated sample was recorded as a background spectrum. Adsorption of pyridine on the sample was then carried out at 150°C for 1 h. Desorption of pyridine was performed under vacuum at different temperatures (200°C , 300°C , 400°C) and the IR spectra was measured at 25°C . The concentrations of the Brønsted acid sites (BAS) and the Lewis acid sites (LAS) were calculated from the integration of the 1540 and 1450 cm^{-1} intensity bands, and the corresponding molar extinction coefficients used were $\epsilon_{1540 \text{ cm}^{-1}} = 0.059 \text{ cm}^2 \cdot \text{mmol}^{-1}$ and $\epsilon_{1450 \text{ cm}^{-1}} = 0.084 \text{ cm}^2 \cdot \text{mmol}^{-1}$ ([Datka, 1981](#)). The results were obtained by the Lambert–Beer equation.

CO chemisorption analyses were obtained at room temperature using an Autochem 2910 Micromeritics by the CO pulse chemisorption method. The catalysts were reduced in situ at 300°C with hydrogen; after the reducing procedure, catalysts were flushed with He. The CO pulse chemisorption measurements were performed by introducing 10% CO in helium. The dispersion was calculated by

using a stoichiometry of $\text{CO}/\text{Pd} = 1$ and assuming Pd particle as a sphere.

2.3. Deoxygenation reactions

Deoxygenation reactions were performed using soybean free fatty acid as feedstock. It was obtained from the non-catalytic hydrolysis of the degummed soybean oil. The composition of the soybean fatty acid was determined by gas chromatography (methodology described in [Section 2.4](#)). It is composed by a blend of the following free fatty acids (wt.%): 10.3% of palmitic acid, 3.4% of stearic acid, 26.3% of oleic acid, 57.0% of linoleic acid and 3.0% of linolenic acid.

A typical deoxygenation reaction was carried out using 25 g of soybean free fatty acid and 2.5 g of catalyst, added in a batch Parr® reactor (240 mL). The catalyst was added to the fatty acid, the reactor was properly closed and H_2 pressure was increased to 10–40 bar. The reactions were performed at 300°C for 6 h. Since the atmosphere in the reaction vessel was always rich in H_2 (high H_2 pressures) and Pd is easily reduced from PdO to Pd^0 , the catalysts were not previously reduced. After 6 h, reaction mixture was solubilized in heptane and filtered for catalyst removal. Solvent was removed using a rotary evaporator and the reaction products were analyzed by gas chromatography.

2.4. Analysis

The feedstock was characterized by dissolving 0.05 g of sample in 1 mL of heptadecanoic acid solution ($10 \text{ mg} \cdot \text{mL}^{-1}$ in heptane). Samples were analyzed in a gas chromatograph (Shimadzu GC-2010) equipped with Carbowax column ($30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$) and a flame ionization detector (FID). $1 \mu\text{L}$ of the sample was injected and the carrier gas (H_2) flow rate was $1.9 \text{ mL} \cdot \text{min}^{-1}$. The analysis were carried out at 200°C isothermal, with injector and detector temperatures at 250°C with a split ratio of 1:50.

Typically, the reaction products had to be dissolved in pyridine and silylated with MSTFA (N-methyl-N-(trimethylsilyl)trifluoroacetamide) in order to be analyzed by a gas chromatography technique. Generally 100% of MSTFA was added to the sample. After the addition of the silylation agent, the samples were kept in an oven at 60°C for 30 min. The internal standard eicosane ($\text{C}_{20}\text{H}_{42}$ – $10 \text{ mg} \cdot \text{mL}^{-1}$ in pyridine) was added for quantitative calculations. Samples were analyzed in a gas chromatograph (Shimadzu GC-2010) equipped with a non-polar column (DB5-HT – $15 \text{ m} \times 0.32 \text{ mm} \times 0.1 \mu\text{m}$) and a flame ionization detector (FID). $1 \mu\text{L}$ sample was injected into the GC with an column injection and the carrier gas (H_2) flow rate was $3 \text{ mL} \cdot \text{min}^{-1}$. The injector and detector temperatures were 380°C . The GC oven temperature was programmed as follows: $1^\circ\text{C} \cdot \text{min}^{-1}$ ramp from 25°C to 50°C ; 1 min soak at 50°C ; $5^\circ\text{C} \cdot \text{min}^{-1}$ ramp from 50°C to 380°C and 10 min at 380°C . Conversion was calculated as described in Eq. (1).

$$C(\%) = \frac{(\sum P) - A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V}{m} \times 100\% \quad (1)$$

where:

$\sum P$	sum of the areas of the products (hydrocarbons and oxygenated products);
A_{IS}	area corresponding to internal standard (eicosane);
C_{IS}	concentration of internal standard solution ($\text{mg} \cdot \text{L}^{-1}$);
V	volume corresponding to eicosane solution + solvent + MSTFA added to sample (mL);
m	weight of the sample (mg).

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