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Transesterification of vegetal oils catalyzed by oxide nanoparticles.

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Abstract – Titanium, tin and zinc oxide nanoparticles were synthesized by solvothermal method. The powders were analyzed by X-ray diffraction, Raman spectroscopy, scanning electron microscopy and transmission electron microscopy. Synthesis parameters were varied in order to obtain crystalline, single phase and nanostructured materials. Catalytic properties in front of transesterification reaction of vegetal oil and ethanol were analyzed by nuclear magnetic resonance. A systematic study of an optimal analysis route was made.

The search for renewable fuels is a very important subject due to its direct influence on economy and environment. Diesel oil is the most utilized fuel in the world and lots of efforts are made currently for its substitution by a cheaper and environment most friendly combustible. Transesterification reaction between vegetal oils and alcohols produce fat acid esters, which are substitute for diesel oil with all advantages off renewable fuels. The key reactant in this reaction system is the catalyst, necessary to promote the formation of biodiesel. Generally, sodium or potassium hydroxides are used, but the presence of small amounts of water must promote soap formation and made impracticable using this product. So, new catalysts are necessary in order to allow the fabrication of biodiesel in large scales. Oxide nanoparticles are promising substitutes for hydroxides because they have a large surface area and also prevent soap formation, since no sodium is present in the reaction medium. The aim of this work is to synthesize and characterize titanium oxide, tin oxide and zinc oxide nanoparticles by solvothermal method and also test their catalytic activity in front the transesterification reaction of corn oil and ethanol.

The solvothermal method utilized in this work was similar with that developed by Niederberger and co-workers [1]. In summary, the metal precursor is dissolved in benzyl alcohol and the resulting solution receives a heat treatment in order to promote nanoparticles formation. Titanium isopropoxide, tin chloride and zinc acetate were used as precursors for TiO_2, SnO_2 and ZnO, respectively. After the heat treatment, the colloidal suspensions were centrifuged to separate the oxide, and the powders were washed with THF. After washing, the nanoparticles were dried on a hot plate and characterized. Those powders were analyzed by X-ray diffraction, Raman spectroscopy, scanning electron microscopy and transmission electron microscopy. Catalytic activity of these oxides was tested with corn oil and ethanol, the most abundant alcohol in Brazil. The ratio between vegetal oil and catalyst were varied in order to find the optimal conditions for transesterification process. The ratio between corn oil and ethanol was varied too. The resulting mixture received a heat treatment in order to promote transesterification reaction. Reaction time and temperature were also studied to find the optimal conditions of biodiesel formation. After the time of reaction, an aliquot of the reaction medium was analyzed by nuclear magnetic resonance to determine the amounts of oil and biodiesel and, consequently, the process yield.

XRD analyses showed that all powders are crystalline single phase nanoparticles, with average crystallite size of 8nm, as calculated by Scherer's equation and verified by electron microscopy. As observed in the literature, solvothermal synthesized nanoparticles are non-agglomerated and have a narrow size distribution. An intensive NMR study was developed in order to obtain quantitative measurements. A calibration curve with $R^2 = 0.998$ was observed in analyzing oil-biodiesel known mixtures. With this curve, it was possible to quantify the reaction yields as a function of reaction time and temperature.

In summary, titanium, tin and zinc nanoparticles were successfully prepared by solvothermal method. The catalytic activity of these materials, in front of transesterification reaction of vegetal oils, was verified by a new nuclear magnetic resonance method.

Reference

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