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TiO₂, SnO₂ and ZnO nanoparticles: a catalytic study

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Abstract – Titanium, tin and zinc oxide nanoparticles were synthesized by the polymeric precursor method. The powders were analyzed by X-ray diffraction, Raman spectroscopy and scanning electron microscopy. Catalytic properties in front of transesterification reaction of vegetal oil were analyzed by nuclear magnetic resonance.

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 of vegetal oils can produce a substitute for diesel, 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 synthesize and characterize titanium oxide, tin oxide and zinc oxide nanoparticles by the Pechini method and also test their catalytic activity in front the transesterification reaction of corn oil and ethanol.

The Pechini method consists in dissolving citric acid in water, followed by the complexation of metallic cations by this policarboxilic acid. Titanium isopropoxide, tin chloride and zinc acetate were used as precursors for TiO₂, SnO₂ and ZnO, respectively. After complete dissolution, ethyleneglycol was added and a polymeric resin was obtained. This resin was heat treated at 350°C for 30 min. and an amorphous coal was formed. This coal received a heat treatment at 500 and 900°C to promote crystallization of the desired materials. Those powders were analyzed by X-ray diffraction, Raman spectroscopy and scanning 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 resulting mixture of oil and biodiesel was analyzed by nuclear magnetic resonance, with an optimized analyzes routine for this quantitative measurements.

XRD analyses showed that all powders are crystalline single phase nanoparticles, with average crystallite size of 80nm. An intensive NMR study was developed, with an optimized analyses routine, it was possible to verify, quickly, the catalytic activity of the oxide nanopowders.

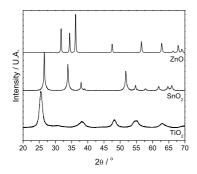


Figure 1: X-ray diffraction patterns of TiO_2 , SnO_2 and ZnO nanoparticles.

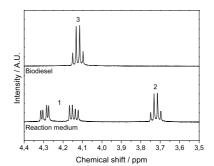


Figure 2: Nuclear magnetic resonance spectra of the reaction medium and the biodiesel.

[1] Morgenstern, M.; Cline, J.; Meyer, S. & Cataldo, S. Energy & Fuels 20 (2006) 1350.