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Catalytic activity of CaO, ZnO, $CaTiO_3$ and $SrTiO_3$ in biodiesel production.

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Abstract – Transesterification of vegetable oils is the best way to obtain the so called biodiesel. A known problem of biodiesel production is the soap formation when sodium hydroxides are used as catalyst. In this work, we present a series of catalytic tests realized in order to substitute the hydroxide for a solid metallic oxide catalyst. It was observed that calcium oxide nanoparticles had satisfactory catalytic activity when submitted to the same conditions of NaOH homogeneous catalyst.

The idea of using vegetable oils as fuel comes from the end of nineteenth century, with Rudolph Diesel. Fuels of vegetable origin have some advantages in comparison with petroleum based fuels, as to be renewable, less toxic, biodegradable, and have lower sulfur contend. In Brazil, ethanol appears as a great substitute for gasoline in combustion based engines. However, for compression based engines, there is not yet a substitute for diesel oil made from vegetable resources produced in the same scale of ethanol. Currently, much research is achieved in order to turn possible the production of biodiesel in commercial scales.

Due to its high viscosity, vegetable oils cannot be used directly on diesel engines. The most common way used currently in order to obtain biodiesel is through the transesterification of those oils. Transesterification is the reaction of triglycerides (oil) with an alcohol (normally methanol and ethanol) generating glycerol and methyl or ethyl esters, also known as biodiesel. In this reaction process, it is essential the use of a catalyst, generally a base. The biggest trouble of using bases in this process is the soap formation, in cases which water is present as a contaminant. Soap generation is followed by an emulsion formation, leading to difficulties in separate the pure biodiesel.

Some metallic oxides have basic character surfaces. These oxides, as example calcium oxide, can be used as catalyst in transesterification with some advantages, like no soap generation, easer of removing from reaction media and reusability. As the reaction occurs in the surface of the catalyst, it is very interesting to have solids with high specific surface area, in order to have the biggest possible area by the same amount of solid. Nanoparticles are known by the very small size, which implies in very high specific surface area. So, nanoparticles with basic surfaces are promising materials to be used as catalysts in biodiesel production.

The aim of this work was to synthesize and characterize CaO, $CaTiO_3$, $SrTiO_3$ and ZnO nanoparticles, and test them as catalyst for transesterification reaction. Those oxides were prepared by the complex polymerization method. This method consists in dissolving an policarboxilic acid in water (citric acid) followed by dissolution of the metal precursors ($CaCO_3$, $SrCO_3$, Zinc acetate and titanium isopropoxide). After complete dissolution, a polyalcohol (ethylene glycol) was added, and a polymeric resin is obtained. This resin was heat treated at 350℃ for 30min, generati ng a puff. It was ground in a mortar, and heat treated at 700℃ for 2h in order to obtain the desired materia l. Those materials were characterized by means of X ray diffraction.

Catalytic tests were made by adding certain amounts of corn oil and alcohol (methanol or ethanol) in a closed vessel, together with the oxide. The reaction temperature and time interval were 90℃ and 2h, respectively. It was observed that calcium oxide have the biggest catalytic activity, much bigger than other oxides. Complete reaction was observed in the case of methanol, and 65% yield for ethanol. It is related with the stronger basic character of this oxide in comparison with the other samples studied in this work.