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CATALYSTS FOR GLYCEROL HYDROGENOLYSIS: PRODUCTION OF GLYCOLS FROM BIOMASS DERIVATIVES

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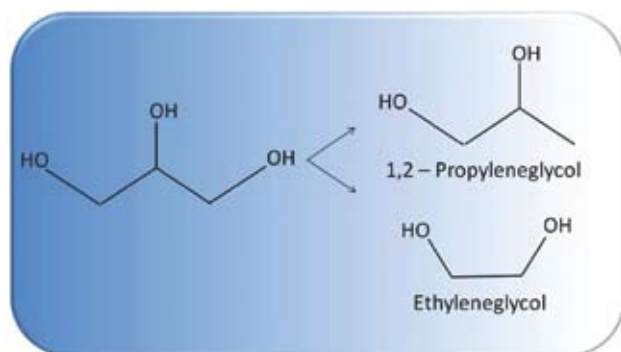Brazilian Synchrotron Light Laboratory (LNLS)

Figure 1. Hydrogenolysis of glycerol producing 1,2-PG and EG

The conversion of biomass and other renewable sources to higher-valued chemicals is one of the strategic goals of the 21th century. It is also a requirement concerning the challenges to be overcome related to environment and energy. Glycerol, a major byproduct of biodiesel production, is one of the main examples of low-cost, large-volume market product that can be used as a starting material for chemical transformation. The "glycerochemistry", which search for routes to process glycerol into more valuable commodity chemical, has become an intense area of research. An industrially relevant route involves the hydrogenolysis of glycerol to 1,2-propylene glycol (1,2-PG) and ethylene glycol (EG) (Figure 1). Both chemicals are widely used for manufacturing important products, from fibers to antifreeze and pharmaceuticals. In the hydrogenolysis reaction, hydrogen gas reacts with glycerol in the presence of a catalyst in several coupled steps, producing intermediates that are finally converted to EG or 1,2-PG. It is a complex reaction that is usually carried out under high pressure of hydrogen (500-1050 psi), high temperature (180-2500C) and for long reaction times (4-20 h), and alternatives routes and optimized catalysts are still desirable for large scale applications. As part of the partnership between Brazilian Synchrotron Light Laboratory (LNLS) and OXITENO S/A, the presented project co-funded by FAPESP aims the development of selective catalysts for hydrogenolysis of glycerol to glycols and the comprehension of the physicochemical characteristic that determine their performance. One of the main parameters guiding this work is the optimization of the selectivity to EG or 1,2-PG in a batch reactor, taking into account requirements for scaling up process. Studies on model systems and reactions supported by advanced characterization of catalysts using synchrotron techniques and electron microscopies will help to speed up the understanding of the system.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The control of glycol selectivity to 1,2-PG or EG requires the deep understanding of the reaction mechanism behind the glycerol hydrogenolysis. Although several works can been found on maximizing the selectivity for 1,2-PG [1] only in the last couple of years a good compromise between conversion and selectivity to EG has being achieved [2] . The main drawback is the uncontrolled C-C bond cleavage that may lead to a high percentage of gas products. For 1,2-PG production, Cu-based catalysts have presented good results while for EG production, Ru/C, transition-metal carbides and Ni-Raney are the most promising alternatives.

In the first year of the project the main effort was focused on the installation of the infrastructure required for catalytic tests. The assembled catalytic unit is composed by a batch reactor (Parr Instruments) of 300 ml, maximum operation pressure of P=1900 psi, temperature T=3500C and stir rate R= 1800 rpm, fed by H_2 from a P-controlled tank. The parameters of the reactor (P, T, rpm) as well as the pressure of the H_2 tank can be controlled remotely. For reaction products analysis we installed a gas-chromatograph (GC) equipped with FID and TCD detectors. The whole system was project following the set-up installed at OXITENO to promote a routine exchange of information and experience. *Figure 2a* shows the catalytic unit installed at LNLS.

Different catalysts have already been obtained and tested, such as Ru/C, Ni/C, Ni-W_2C and Ni-Raney. A general trend is the tendency for 1,2-PG formation among the liquid products after several hours of reaction. Selectivity to EG has been maximized only at short times and low conversions. *Figure 2b* shows preliminary results for Ni-Raney catalysts. This is in agreement with the main challenge to high production of EG that is to control the excessive cleavage of C-C leading to gas products. Next steps involve the detail analysis of the gas phase products, optimization of reaction conditions using concentrate glycerol solution (closer to industrial need), exploration of model reactions and improvement of Ni-W_2C catalyst synthesis.
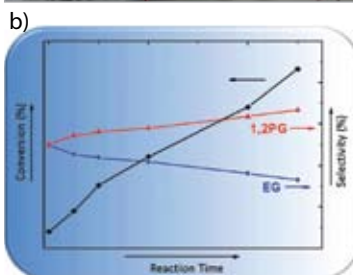
a)

b)

Figure 2. (a) Catalytic unit at LNLS and (b) preliminary results obtained with Ni-Raney catalysts

MAIN PUBLICATIONS

Related to bioenergy, not derived from this project.

Ribeiro RU, Liberatori JWC, Winnishofer H, Bueno JMC, Zanchet D. 2009. Colloidal Co nanoparticles supported on SiO_2: Synthesis, characterization and catalytic properties for steam reforming of ethanol. *Appl. Catal. B*. **91**:670-678.

Rodella CB, Kellermann G, Francisco MSP, Jordão MH, Zanchet D. 2008. Textural and Structural Analyses of Industrial Raney Nickel Catalyst. *Ind. & Eng. Chem. Res*. **47**:8612-8618.

Liberatori JWC, Ribeiro RU, Zanchet D, Noronha FB, Bueno JMC. 2007. Steam reforming of ethanol on supported nickel catalysts. *Appl. Catal. A*. **327**:197-204.

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