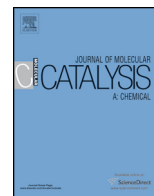




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Green propene through the selective hydrogenolysis of glycerol over supported iron-molybdenum catalyst: The original history

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ABSTRACT

The hydrogenolysis of glycerol, a byproduct of biodiesel production, to propene was studied over supported metallic catalysts. About 100% glycerol conversion was observed for all catalysts, but the selectivity was dependent on the composition. Ru and Pd on activated carbon produced mainly propane and methane/ethane, respectively. Ni/Mo on activated carbon gave mainly propene, whereas Zn/Mo and Cu/Mo supported on activated carbon produced intermediate oxygenated compounds. Fe/Mo over activated carbon presented up to 90% selectivity to propene. This results may be explained in terms of the poor reductibility of the Fe/Mo catalysts, as shown by TPR and XRD experiments. A possible pathway from glycerol to propene involves the formation of acetol, 1,2-propanediol and 2-propanol as intermediates.

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1. Introduction

Catalysis plays an important role in biorefining processes. Enzymes or biological catalysts are key component in many transformation of sugars into fuels and chemicals, whereas several inorganic materials catalyze the conversion and upgrading of biomass. Hydrogenation and hydrogenolysis appears as one of the most important biorefinery processes to use heterogeneous catalysts. Nevertheless, they usually rely on noble metals to achieve good conversion and selectivity. Some metals used in these processes, such as Pt, Pd, Ru and Ir, are considered endangered, as their supply may be in risk in the future due to increasing use, as well as limited available reserves [1]. On the other hand, the chemical industry will still process hydrogenation reactions, as they are key to the production of improved fuels and chemicals. Many biomass-derived feedstock possesses oxygen atoms, which

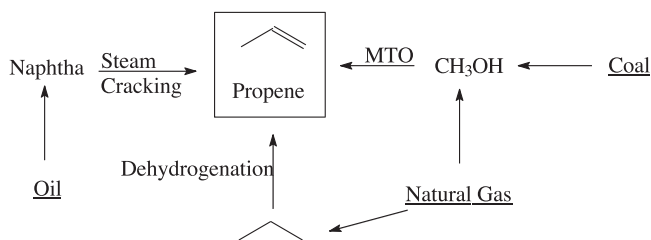
must be partially or totally removed during processing. Therefore, the search for hydrogenation and hydrogenolysis catalysts based on more abundant metals is of prime importance to attain more sustainable biorefinery processes.

Propene is one of the most important chemicals in industry, with global production around 80 million tonnes per year. About 2/3 of the propene produced is directed to polypropylene (PP), which is a thermoplastic with increasing applications. Propene is basically obtained from fossil sources (Scheme 1), with the steam reforming of naphtha being the main process [2]. In addition, propene can also be produced from methanol over acidic molecular sieve catalysts [3]. This is an indirect route of propene from natural gas or coal, because methanol is normally produced from these fossil sources. Propene can still be produced from propane dehydrogenation over noble metal catalysts [4]. However, propane is a minor constituent of natural gas, or is formed in the catalytic cracking of petroleum fractions. On the other hand, the production of propene from renewable feedstock is poorly studied, differently from ethene, which can be obtained through the dehydration of bioethanol [5]. Thus, the development of green propene, from biomass-derived feedstock, is highly desired and pursued in the chemical industry.

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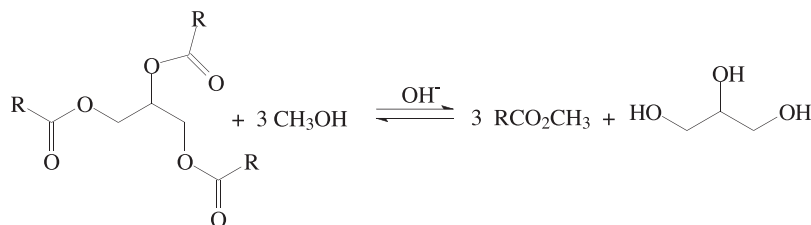


Scheme 1. Main industrial routes to propene from fossil sources (oil, coal and natural gas).

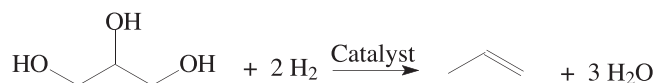
Biodiesel is an important biofuel used mainly in Europe and South America. In Brazil, there is a mandatory blend of 7% biodiesel in the regular diesel and an increase in this percentage is being considered for the next years. The transesterification of oils and fats is the main industrial process for the production of biodiesel [6]. It involves the reaction of a triglyceride with excess methanol, in the presence of a basic catalysts, to afford three molecules of fatty acid methyl esters, the biodiesel, and a molecule of glycerol, which accounts approximately to 10 wt% of the total mass of the system (Scheme 2). The use of glycerol as a renewable feedstock in biorefinery processes has motivated many studies in the recent years [7–10]. Hydrogenolysis of glycerol is one of the main studied processes. Different metal catalysts can be used, with 1,2 and 1,3-propanediols being the main target products [11–13]. Some studies reported that, at more severe conditions, isopropanol and *n*-propanol could also be observed [14,15]. This fact could open a possibility of developing a glycerol to propene route, because dehydration of propanols over acidic catalysts would afford propene as major product.

Aiming to develop a technological route to produce propene from renewable raw materials, we have began an extensive study on glycerol hydrogenolysis, which ultimately led to the development of bimetallic catalysts for the selective production of propene. The initial results were published on the patent literature [17,18]. Thereafter, Yu et al. reported a selective glycerol hydrogenolysis to *n*-propanol over Iridium supported catalysts. The coupling of this metal catalyst with acidic ZSM-5 zeolite may provide a technological route to produce propene from glycerol, in high conversion and selectivity [16]. Nevertheless, Iridium is considered an endangered element and faces serious threat, due to limited availability and increasing use. In addition, the process is carried out in two steps, using two different catalysts, which may increase the operational costs. Thus, the development of an Ir-based catalyst may not be economically and environmentally feasible for the production of green propene, a major chemical commodity.

Here, we report the original history behind the development of the iron/molybdenum-based catalyst for the selective hydrogenolysis of glycerol to propene, as reported in the previous patents [17,18] (Scheme 3). Molybdenum is highly used in oil refining, as a major component of hydrotreating catalyst to remove sulfur and nitrogen from diesel and kerosene, but there is no serious danger of supply of this element in the forthcoming years. Iron is the main catalyst for ammonia production and highly abundant on Earth.



Scheme 2. Transesterification of triglycerides to produce biodiesel and glycerol.



Scheme 3. Hydrogenolysis of glycerol to propene.

Hence, a technological route to propene from glycerol, relying on sustainable metal catalysts, can be of great relevance for developing a biorefinery process based on oils and fats.

2. Experimental

The catalysts were prepared by successive impregnation of the metals over an activated carbon (AC) support. Initially, molybdenum was impregnated by a slurry method [19]. About 10 g of activated carbon were placed in a 250 mL Erlenmeyer and 1.5 g (10.6 mmol) of MoO₃ were mixed together with 100 mL of deionized water. The system was kept stirring at room temperature for 24 h and then, the water was evaporated at 70 °C under reduced pressure. In the sequence, a specific mass of Ni(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O or Fe(NO₃)₃·9H₂O, corresponding to 6.93 mmol of the metals, were dissolved in the minimum amount of deionized water and put in contact with the solid obtained upon the Mo impregnation of the AC. Then, a solution of about 150 mL of 30 wt% ammonium hydroxide were added dropwise to precipitate the metal hydroxide. At the end, the system was stirred at room temperature for 24 h and then subjected to water evaporation at 70 °C and reduced pressure. The final solid was calcined at 450 °C for 2 h (rate of 10 °C min⁻¹). The atomic ratio of the catalysts were 0.4 considering the amount of the metal divided by the amount of the metal plus Mo.

The catalysts were characterized by temperature programmed reduction (TPR), X-ray diffraction (XRD), N₂ physisorption and acidity, which was measured by *n*-butylamine termodesorption (TPD), according to a previous publish method [20]. The chemical composition was measured by X-ray fluorescence (FRX).

The catalysts were evaluated in a fixed bed flow unit at atmospheric pressure. The catalysts were initially reduced on 40 mL min⁻¹ of H₂ at 550 °C for 30 min (rate of 10 °C min⁻¹). Then, the temperature was decreased to 300 °C and a solution of 90 vol% of glycerol in water was introduced into the H₂ gas flow (40 mL min⁻¹) by means of a syringe pump. The weight hour space velocity (WHSV) in relation to the glycerol was 5.4 h⁻¹ in many experiments. The products were analyzed by on-line capillary gas chromatography equipped with a methyl silicone column (100 m × 0.15 mm × 0.5 μm) using a flame ionization detector.

Commercial Pd and Ru supported catalysts were also tested in the hydrogenolysis of glycerol. These catalysts were kindly provided by Evonik and have 5 wt% of the metal supported over activated carbon.

3. Results

We began the studies toward a selective process of glycerol hydrogenolysis to propene using the commercial Ru and Pd cat-

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