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Effect of niobia and alumina as support for Pt catalysts in the hydrogenolysis of glycerol

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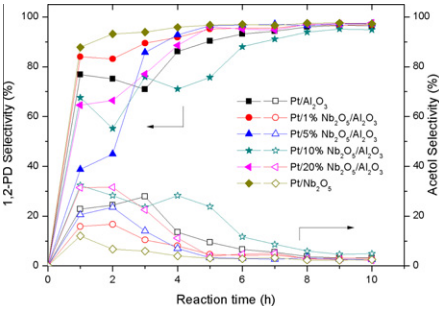
HIGHLIGHTS

- ▶ Niobia–alumina mixtures can be used as support for active hydrogenolysis catalysts.
- ▶ Glycerol is converted to 1,2-propanediol with yield of 78.8% and selectivity of 95%.
- ▶ Decorating effect of NbOx onto the metallic particles activate C—OH bond.

GRAPHICAL ABSTRACT



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ABSTRACT

Catalysts of Pt/x%Nb_2O_5/Al_2O_3 (where x = 0, 1, 5, 10, 20 or 100) + Amberlyst 15 were evaluated through the reaction of glycerol hydrogenolysis in a batch system at 413 K and 50 bar of H_2, with the aim of producing 1,2-propanediol. The supports were characterized by X-ray diffraction (XRD), temperature programmed reduction (TPR), scanning electron microscopy (SEM) and nitrogen adsorption (surface area – BET and pore size and volume – BJH). Niobia is present as islands on alumina surface, which reduces the interaction between these oxides and favors the creation of Brønsted acidic sites, so that the observed behavior is similar to pure niobia. All systems showed a high yield and selectivity for the production of 1,2-propanediol. The presence of niobia as a support leads to a highly active and selective catalyst for 1,2-propanediol production. The change in the behavior of the active metal can be related to the SMSI effect, inherent to systems containing niobia as support.

1. Introduction

Biofuels are in the center of the world discussion about energy, due to the necessity to decrease the global dependence of the non-renewable energy sources. Nowadays, approximately 85% of the commercial energy of the world comes from the fossil sources. Thus, biodiesel from vegetable oil has recently emerged as the eventual replacement of petroleum diesel, mainly due to the environmental benefits obtained from the use of biofuel [1].

Currently, biodiesel is produced from oil plants by a transesterification process involving a short chain alcohol (methanol or ethanol) and typically an alkaline homogeneous catalyst. Biodiesel production has grown significantly in the last years. At the same time, there was a proportional increase in derivative products such as glycerol. It was estimated that the global production of glycerol from biodiesel will be around 1.2 million ton by 2012 [2]. In Brazil, production was about 260,000 tons in 2010, an amount which tends to increase with the implementation of B5 (5% biodiesel added to petrodiesel). On the other hand, the consumption of glycerin in Brazil, mostly for personal care, cosmetics and food usage, is about 30,000 tons per year [3]. Despite the multiple applications of this product, the price has dropped and it is estimated that there will be a significant surplus in the coming years, so the need for new applications of crude glycerin has become essential to establish a complete cycle of biodiesel production [1,4]. Thus it

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has been evaluated others potential uses for the crude glycerol from biodiesel and glycerol conversion in chemical products with higher added value. Chemical processes such as oxidation, dehydration, halogenation, etherification, esterification, pyrolysis and hydrogenolysis of glycerol has been presented as viable alternatives [5].

The hydrogenolysis of glycerol is a catalyzed reaction, where heterogeneous systems containing metals such as Ru, Pd, Pt, Cu or Ni supported has been presented as a satisfactory route to obtain ethylene glycol and propanediols [6–11]. Bienholz et al. [12] and Sánchez et al. [13] evaluated the performance of different copper catalysts in liquid phase and was checked high selectivity to 1,2-propanediol. Musolino et al. [14] described a method to selective conversion of glycerol to 1,2-propanediol using as catalyst Pd/Fe_2O_3 reduced "in situ", giving full conversion with 94% of selectivity to 1,2-propanediol.In previous studies [15,16] some of us evaluated the activity and selectivity of Pd, Pt and Ru supported catalysts in hydrogenation reactions, Pt among which proved to be very active and selective.

Previous works showed that the glycerol hydrogenolysis occurs through dehydration of glycerol (first step). At this stage it is possible the production of some intermediates, mainly 1-hydroxypropane-2-one (acetol) which is subsequently hydrogenated (second step) to 1,2-propanediol (Fig. 1) [7,8,17]. An important technical barrier is the development of a selective catalysts to 1,2- or 1,3-propanediol, which should differentiate C—C from C—O bonds and, by this way, to carry out the hydrogenolysis reaction selectively. Otherwise, ethyleneglycol could be formed over the propyleneglycols and acrolein can be formed from acetol [18,19]. Selective hydrogenolysis of glycerol to 1,2-propanediol requires the cleavage of C—O bond by hydrogen, without attacking C—C bonds from the glycerol molecule [20]. Some researchers have demonstrated that the use of platinum as an active metal present good selectivity to 1,2-propanediol in the reaction of glycerol hydrogenolysis [8–10].

Another possibility of active catalysts in these reactions is represented by the active species supported on niobia. Niobium-containing catalysts have attracted great interest in heterogeneous catalysis as a catalyst and support for a variety of important reactions. Niobia has a high acidity, which, curiously, is maintained in aqueous environments and this particular property is favorable to the dehydration reaction in aqueous phase [21–23]. Compounds of niobium have some special properties besides acidity, which are not shown by the compounds of neighboring elements in the periodic table, like strong metal support interaction (SMSI), the promoting effect and redox properties [24,25].

Niobia supported on Al_2O_3 and SiO_2 generate new Brønsted acid sites which are attributed to niobium oxide species (NbO_6, NbO_7 and NbO_8, slightly distorted) present on the support surface [26–29]. Furthermore, the use of an ion-exchange resin as acid catalyst also is attracting great interest to promote the first step of the reaction [7,30].

In this work it will be verified the performance of Pt supported on $x\%Nb_2O_5/Al_2O_3$ (where $x = 0, 1, 5, 10, 20$ or 100) and Amberlyst 15, in the glycerol hydrogenolysis with focus on the selective production of 1,2-propanediol.

2. Experimental

2.1. Synthesis of supports

Niobic acid (CBMM HY-340) was dissolved in 100 mL of oxalic acid under reflux for 4 h [31]. The solution was cooled to room temperature and it was added concentrated ammonium hydroxide until pH ~ 9.5. The complete precipitation of niobium oxalate was achieved after cooling the suspension to 278 K. The solid was separated by filtration and dried at 393 K for 24 h. Nb_2O_5/Al_2O_3 supports were prepared by impregnation over alpha-alumina powder (Sigma–Aldrich, 98%) with an oxalic acid solution of niobium oxalate. Niobia loading were 0%, 1%, 5%, 10% and 20% (w/w). The samples were dried at 393 K and calcined in air at 823 K for 4 h. To obtain pure niobia, niobium oxalate was calcined at the same conditions.

2.2. Synthesis of catalysts

The catalysts were prepared by the conventional incipient wetness method, using an aqueous solution of $Pt(NH_3)_4Cl_2 0{,}68H_2O$ (Aldrich, 98%), followed by drying at 393 K for 24 h and calcination treatment for 4 h at 573 K, under 50 mL min^{-1} of synthetic air flow. Immediately before the catalytic test, the solid was reduced for 2 h at 673 K under H_2 atmosphere.

2.3. Thermal programmed desorption of ammonia

NH_3 temperature programmed desorption (TPD) was used to determine the acid properties of the catalytic materials. The experiments were conducted on a Quantachrome ChemBet 3000 device. The catalysts (100 mg) were pretreated at 523 K for 30 min and then cooled to 373 K under a He flow. The pretreated samples were saturated with 5% NH_3/He for 1 h at 373 K, with subsequent flushing with helium at 373 K for 2 h to remove the physisorbed ammonia. TPD analysis was carried out from 373 K to 873 K at a heating rate of 10 K min^{-1}.

2.4. Temperature programmed reduction

The reduction characteristics of the catalysts were studied by temperature programmed reduction (TPR) with the same apparatus used to NH_3–TPD measurements, on a quartz reactor. Before analysis, the catalysts (110 mg) were dried in situ at 383 K for 4 h under 50 mL min^{-1} of nitrogen flow and cooled to room temperature. After pretreatment, the temperature was raised from room temperature to 1200 K at a rate of 10 K min^{-1} in a 5% H_2/N_2 flow.

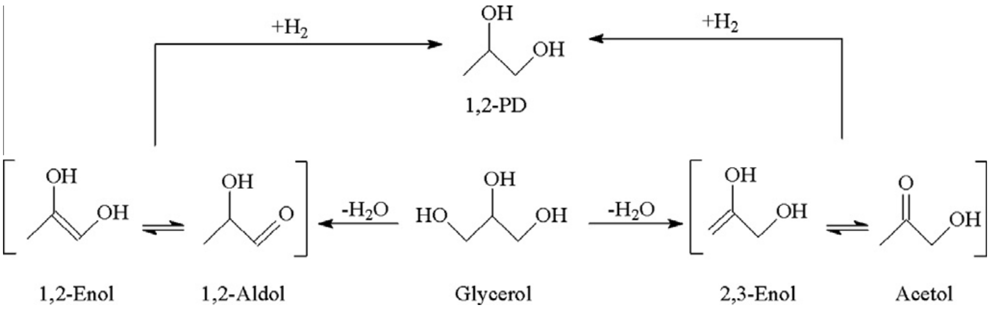

Fig. 1. Possible routes for the glycerol hydrogenolysis. Adapted from [17].