

Ni/CeO₂ as catalyst for glycerol hydrogenolysis without external H₂ supply: the role of synthesis conditions

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Introduction

Aqueous phase processes at high pressure are considered one of the most promising thermochemical processes to valorize wet residual streams, in order to produce value-added chemicals. Among them, glycerol hydrogenolysis (HG) has been intensely studied. Although many different catalytic systems for HG have been studied in the last years (Dasari et al. 2005; Gandarias et al. 2011; Liu et al. 2018; Sun et al. 2016), the Ni/CeO₂ catalytic system has not been so deeply performed in liquid phase.

Purpose of the work

This work studies the hydrogenolysis of glycerol without external H₂ supply as a pathway to obtain value-added chemicals using Ni/CeO₂ catalysts. Different synthesis parameters were changed, such as the support calcination temperature, the catalysts calcination temperature and the Ni content, in order to determine their influence on the catalytic activity. In this process, 1,2-propanediol and ethylene glycol are produced, compounds which are valuable due to their use in chemical synthesis, antifreeze fluids and others.

Methodology

Catalysts: preparation and activity tests

Ni/CeO₂ catalysts were prepared by the incipient wetness impregnation method. First of all CeO₂ support was obtained by calcination of Ce(NO₃)₃·6H₂O at 500 and 700 °C, so as to study the support calcination temperature. The catalysts were loaded with different Ni amounts (10, 15 and 20 wt.%) and calcined at 600, 700 or 800 °C.

The activity tests were developed under N₂ atmosphere in a continuous lab scale fixed-bed reactor (PID Eng&Tech) using 1 g of catalyst at 227 °C, 33 bar during 3 hours. A 5 wt.% glycerol aqueous solution was pumped from an HPLC pump

at 1 ml/min. The gas products were analyzed by an online micro-GC and the liquids were analyzed afterwards by GC/FID and TOC. These liquid products were collected every each hour, in order to study the activity trend with time.

Different characterization techniques were employed to study the physico-chemical properties of the catalysts: XRD, N₂-physisorption, H₂-TPR, NH₃-TPD, SEM, TEM and ICP-OES.

Results and discussion

Catalysts characterization

XRD technique allowed us to determine the crystallite sizes as well as the crystalline phases of the fresh, reduced and used catalysts, confirming only the presence of CeO₂ and NiO or Ni in the fresh and reduced ones, respectively. Moreover, the XRD analysis of the used catalysts displayed very important information: the catalytic structure suffered severe changes after the experiments due to the transformation of CeO₂ phases into Ce carbonates structures.

N₂-physisorption was performed to study the textural properties of the catalyst, showing how the specific area decreased as the calcination temperature or the Ni content was raised.

H₂-TPR essays determined the optimal reduction temperature of the catalysts to active it and was also determined to establish possible interactions between the active phase and the support.

The acidity of the catalysts was studied by NH₃-TPD, which allowed us to determine the total acidity and the corresponding strength of acid sites.

Meanwhile, the metal dispersion was obtained by H₂-chemisorption, showing that all these catalysts present a very low metal dispersion. This fact was also corroborated by the SEM and TEM images, which revealed, in the case of the fresh catalysts, big

NiO clusters anchored on the CeO₂ surface. In addition, the SEM images of the used catalysts confirmed the XRD results for these samples, showing very clear and crystalline Ce carbonates structures.

ICP-OES analyses were performed with two objectives. Firstly, it allowed establishing the real Ni content on the catalysts and confirming in all cases the excellent Ni incorporation onto the CeO₂ support. Secondly, the analysis of the liquid products to determine the amount of leached metal to the liquid phase, which showed very low Ni and Ce concentration values.

Activity tests

The activity test performed corroborated that these catalysts are very selective to liquid products. The gas products amount was very low (C conversion to gas lower than 5 %), mainly formed by H₂ and CO₂. The majoritarian liquid products were 1,2-propanediol (1,2-PDO), acetol, ethylene glycol and ethanol.

It was also shown that a change in the synthesis conditions leads to a change in the global catalytic activity and also in the selectivity towards certain liquid compounds. This is related with the changes in their physico-chemical properties, such as the acidity and the Ni crystallite size, which have a great influence on the reaction mechanism.

First of all, a higher CeO₂ calcination temperature implies a decrease in the catalytic activity and in the selectivities towards 1,2-PDO and ethylene glycol.

Meanwhile, an increase in the catalyst calcination temperature presented different trends. Actually, the global activity increased from 600 to 700 °C and decreased again at 800 °C. However, the selectivities towards 1,2-PDO and ethylene glycol decreased as temperature was raised.

Finally, increasing the amount of Ni implies very interesting changes in the catalysts properties. A first increase from 10 to 15 wt.% involved a decrease in the global activity, followed by a decrease of this variable when the Ni was increased up to 20 wt.%. These changes are related to the changes on the acidity and the metallic dispersion of the catalysts. However, the selectivity towards 1,2-PDO and ethylene glycol was improved when increasing the amount of Ni.

Conclusions

The aim of this work was, firstly, to test the activity of the Ni/CeO₂ catalytic system in the hydrogenolysis of glycerol without external H₂ supply and also to study the influence of the synthesis parameters on glycerol conversion and selectivity towards liquid products.

It was tested that these catalysts are suitable for this process. Despite the fact that the catalytic structure suffered changes after the reaction, no loss of activity was observed due to this or to leached metal.

Changing the synthesis conditions implied changes on the physico-chemical properties of the catalysts which are directly related to their global activity and their selectivity toward the most relevant liquid products, 1,2-PDO and ethylene glycol.

Acknowledgements

The authors wish to express their gratitude to the Aragon Government (GPT group) and the Research Projects ENE2013-41523-R and CTQ2017-86893-R (AEI/FEDER, UE) for providing financial support. The authors would also like to acknowledge the use of Servicio General de Apoyo a la Investigación-SAI of the Universidad de Zaragoza. In addition, Clara Jarauta-Córdoba would like to express her gratitude to the Spanish MINECO for the predoctoral grant (BES-2014-069165) awarded.

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