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Valorization of glycerol from the biodiesel industries as a renewable substrate for producing DHA using microporous zeolites modified with noble metals.

E. Diguilio, E.D. Galarza, M.S. Renzini, L.B. Pierella
Centro de Investigación y Tecnología Química (CITeQ - UTN - CONICET), Cordoba, Argentina

Aim

Glycerol (Gly) is an important renewable resource derived from biodiesel industries and it is used in food, cosmetic and pharmaceutical applications. Due to increasing production of biodiesel the price of the main by-product has decline, due to this last years has had special attention.
Gly is a platform molecule to obtain different high value fine chemicals like aldehydes, ketones and organic acids, including dihydroxyacetone (DHA), glyceric acid, glycolic acid and lactic acid.
By liquid phase oxidation of Gly under mild conditions, using microporous zeolites modified with the incorporation of noble metals such as Pt and Au, it was possible to obtain an interesting production of DHA.

Methods

The Na-ZSM-11 zeolite (Si/Al = 17) was obtained by known methods of hydrothermal crystallization, using tetrabutylammonium hydroxide as a structure directing agent [1]. The ammonium form of the zeolite (NH4-zeolite) was prepared by ion exchange of the as-prepared Na-zeolite form with 1 M ammonium chloride solution at 80° C for 40 h. The noble metals were incorporated by wet impregnation with loading metal of 2 wt%, followed by desorption in nitrogen flow and calcination at 500º C for 8h.
Catalytic performance was evaluated in liquid phase, in a 25 ml glass reactor using aqueous solution of glycerol (0.5 M) at atmospheric pressure with constant stirring. The temperature was kept at 60º C for 6 h, employing air or H2O2 as oxidizing agents, 200 mg of catalyst was used in a typical experiment.

Results

Using air as the oxidizing agent and reaction conditions mentioned above it was obteined Gly conversion of 26 wt% using Pt- ZSM-11, without generating the desired product DHA. This behavior due to the oxidation of the primary hydroxyl group of Gly, which was evidenced by the presence of glyceraldehyde and glycolic acid in the reaction products.
Subsequently we proceeded to use H2O2 as oxidizing agent obtaining DHA with a selectivity of 33 wt% and Gly conversion 42 wt% over Pt- ZSM-11. When Au was deposited on Pt-ZSM-11 by co-impregnation, Gly conversion was similar (40 wt%) but DHA selectivity decrease sharply (10 wt%), possibly because Au could be able to block specific active Pt sites, allowing the oxidation of primary hydroxyl group of glycerol that was evidenced by the reaction products [2].

Conclusion
Pt-ZSM-11 catalyst exhibited an interesting behaviour for Gly oxidation reaction, using H_2O_2 as oxidizing agent. This performance could be related with dissolved oxygen during H_2O_2 decomposition in the reaction medium, generating a greater amount of O_2 available to oxidize glycerol. Because of that, this oxidizing agent proved to be more effective than air in the oxidation reaction of glycerol in mild condition, in a base free medium.

References:
[1] P. Chu, US Patent No. 3709979 , (1972), “Crystalline zeolite ZSM-11”
[2] A. Villa, S. Campisi, C. E. Chan-Thaw, D. Motta, D Wang, L. Prati,, (2015), Bismuth modified Au-Pt bimetallic catalysts for dihydroxyacetone production

Authors

First author: Eliana Diguilio
Presented by: Eliana Diguilio
Submitted by: Eliana Diguilio