

Acid-Catalyzed Dehydration of Glycerol to Acrolein and Acrylic Acid.

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Introdução

Biodiesel is a major biofuel used in Brazil, with a mandatory blend of 7% in the regular petrodiesel in the present days. It is normally produced through the basic-catalyzed transesterification of oils and fats with methanol [1], affording glycerol as byproduct in approximately 10 wt%.

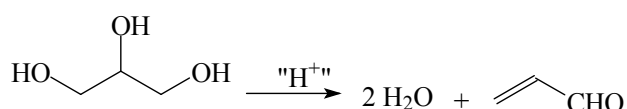
This surplus of glycerol coming from the biodiesel production has motivated new uses, especially as a renewable feedstock for the chemical industry [2].

The acid-catalyzed dehydration of glycerol can afford acrolein as one of the main products. Acrolein is an important intermediate in the production of acrylic acid and methionine. Nowadays, acrolein is industrially produced from fossil sources, through the oxidation of propene over Bi and Mo based catalysts [3]. The development of a green and economically feasible route to acrolein is highly desirable, but many studies show that catalyst deactivation is a major problem [4].

We wish to present our recent results on the acid-catalyzed dehydration of glycerol to acrolein and acrylic acid over catalysts based on niobium, as well as mesoporous silica-alumina materials.

Resultados e Discussão

The conversion of glycerol to acrolein takes place through two consecutive dehydration steps, both catalyzed by the acid sites of the catalysts (Scheme 1).



Scheme 1. Acid-catalyzed dehydration of glycerol to acrolein.

We studied the dehydration of glycerol over two families of heterogeneous acid catalysts: niobium-based and mesoporous silica-alumina. The first family involved the impregnation of metals, such Co, Mo and V over niobium oxide (niobic acid) and niobium phosphate. The second family involved the synthesis of mesoporous MCM-41 silica-alumina materials.

The reactions were carried out in a continuous flow, fixed bed catalytic unit. The glycerol was introduced in the gas flow (N₂ or air) by means of a syringe pump. The reaction temperature was typically 300 °C and the products were analyzed on line by gas chromatography using flame ionization detector (FID). Table 1 shows some results of glycerol conversion and acrolein selectivity. Some catalysts did not present significant deactivation and showed formation of acrylic acid when the reaction was carried out in air.

Tabela 1. Acid-catalyzed conversion of glycerol.

Catalyst	Conversion (%)	Acrolein Selectivity (%)
Nb ₂ O ₅	100	75
Mo-Co/Nb ₂ O ₅	100	80
NbOPO ₄	100	75
V/NbOPO ₄	100	80
Al-MCM-41	99	60

Conclusões

Acrolein can be produced in high selectivity upon the acid-catalyzed dehydration of glycerol. Some selected catalysts presented slow deactivation and were also selective to acrylic acid.

Agradecimentos

CNPq, FAPERJ, PRH-ANP, FINEP, CAPES

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