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Catalytic deoxydehydration of glycerol to allyl alcohol with 2-hexanol as H-donor ?
a detailed study of the reaction mechanism

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PURPOSE OF THE ABSTRACT

Introduction

Allyl alcohol is a very promising starting material for a variety of molecules such as acrylonitrile, acrolein and acrylic acid ? all, important intermediates for the chemical industry: The ammoxidation of allyl alcohol to acrylonitrile was reported with high yield (more than 80%) by Guillon et al.[1-2], The selective oxidation of allyl alcohol to produce acrylic acid yields up to 85 % at rather low temperatures (300°C) over MoVOx catalyst.[3] Today, the main bottleneck for these applications lies in the sourcing of allyl alcohol. In fact, currently allyl alcohol is produced by the selective catalytic hydrogenation of acrolein, which is obtained by the selective catalytic oxidation of propylene. Recently we reported the synthesis of allyl alcohol in high yields over an alumina supported Re-catalyst with 2-hexanol as sacrificial hydrogen-donor.[4]

Experimental

For the DODH reaction of glycerol, a Re-catalysts was prepared by an incipient-wetness impregnation using an 75 wt% perrhenic acid aqueous solution (Aldrich) and g-Al₂O₃ as a support. After one hour, the impregnated catalysts was dried at 110 °C for 24 h and then calcined under static air from 110 °C to 500 °C (5 °C / min) for 3 h. The catalytic performance in the DODH reaction as determined using a pressure-resistant glass tube equipped with a magnetic stirring bar was loaded with 100mg of catalyst, glycerol (92 mg, 1 mmol), 100 mg, and 2-hexanol (3.3 mL). The reaction temperature inside the tube was 148 °C and the reaction time 2.5h. The conversion and selectivity was determined by GC analysis using Biphenyl (20 mg, 0.13 mmol) as an internal standard.

Results

The DODH catalyst based on 10 wt% ReOx/Al₂O₃ exhibited full conversion after 4h, yielding up to 76% of allyl alcohol. From the reaction curve (Figure 1), it becomes visible that the selectivity in allyl alcohol increased during the 2 first hours of reaction, suggesting the presence of an intermediate species. With respect to these results, the by-products were more deeply analyzed using GC-MS, allowing notably the identification of hexenes, ethers and acetals (figure 2). The identification of acetals was most surprising. The latter is formed by condensation of glycerol with acrolein, indicating that acrolein is the intermediate species in the DODH reaction. The latter is formed by dehydration of glycerol and then further hydrogenated to allyl alcohol. The significant formation of acetal in the beginning of the reaction can be explained by the fact the role of water. In fact, the acetalization between acrolein and glycerol is an equilibrium reaction, giving water as a co-product. When the amount of water in the reaction mixture is low, the equilibrium is on the side of the acetals. Here, other identified side reactions come into the game: 2-hexanol was found to be dehydrated to various hexenes and condensated to an ether during the reaction. The as-formed water helps to shift the equilibrium of the acetalisation to the reactant side

(formation of acrolein), whereby the selectivity of the final product (allyl alcohol) increased with reaction time. The corresponding mechanism was further validated by using individual reaction with acrolein, water and 2-hexanol.

Conclusion

The DODH reaction of glycerol over a heterogeneous $\text{ReOx}/\text{Al}_2\text{O}_3$ catalyst using 2-hexanol as H-donor showed increasing selectivity in allyl alcohol over reaction time, suggesting the formation of an intermediate. The deep analysis of the reaction mixture revealed the presence of acetals formed from the reaction between acrolein and glycerol. With respect to the equilibrium of this reaction, water was found to play a key-role to.

FIGURES

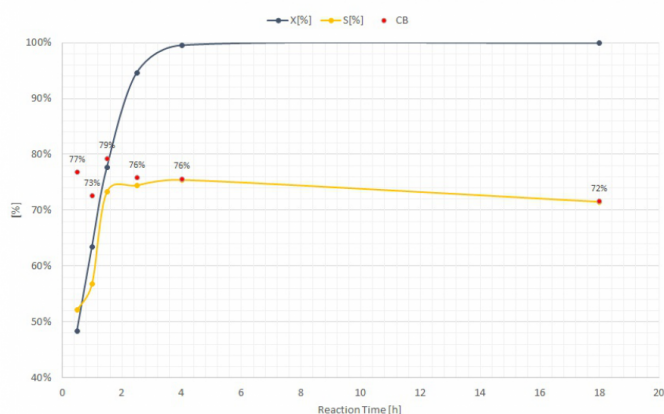


FIGURE 1

Fig1:

Glycerol conversion and allyl alcohol yield observed over the ReOx/Al₂O₃ catalyst as a function of time.

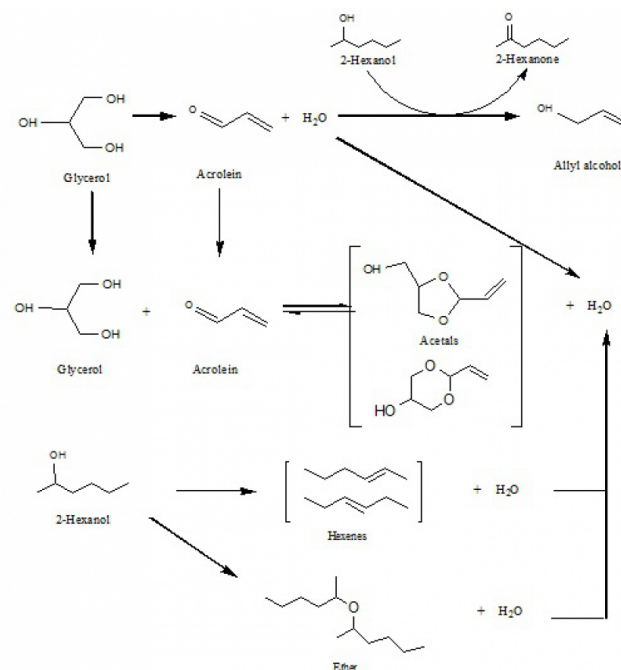


FIGURE 2

Fig2

Proposed mechanism via acrolein as an intermediate

KEYWORDS

Glycerol | Allyl alcohol | DODH

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