Catalytic deoxydehydration of glycerol to allyl alcohol – a promising pathway to a high-versatile platform molecule

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Abstract: Allyl alcohol is a platform molecule with high potential as a starting material for various large scale chemical intermediates such as acrylonitrile and acrylic acid. In this work we report the promising production of allyl alcohol from glycerol (> 90% yield) using Re based catalysts with 2-hexanol as hydrogen donor in continuous flow conditions. Furthermore, the regeneration of the hydrogen donor is shown.

Keywords: Glycerol, DODH, Allyl alcohol.

1. Introduction (11-point boldface)

Ally 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. Hence, for the moment, no sustainable synthesis of allyl alcohol is established. Nevertheless, several renewable sources can be envisaged as starting material for the synthesis of allyl alcohol whereby the most promising one – notably in terms of carbon economy – is the deoxydehydration of glycerol. Since this reaction includes the use of an alcohol as sacrificial hydrogen-donor, the recycling of the latter must also be addressed.

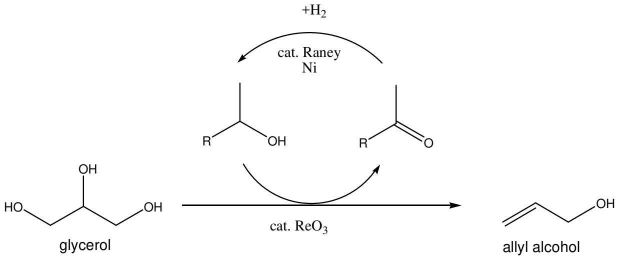

Figure 1. Mechanism for the deoxydehydration of glycerol into allyl alcohol with a sacrificial secondary alcohol and the regeneration of the latter by hydrogenation of the correspondingly formed ketone

2. Experimental

For the DODH reaction of glycerol, alumina supported Re-catalysts with different Re contents were prepared by an incipient-wetness impregnation method using an 75 wt% perrhenic acid aqueous solution (Aldrich) and γ-Al_2O_3 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.

3. Results and discussion

The DODH catalyst based on 10 wt% ReO_x/Al_2O_3 exhibited full conversion after 1h, yielding 91% of allyl alcohol. This yield remained constant upon reuse of the catalyst for three cycles, with yields in the range of 91-93%, meaning that no leaching of Re occurred in between. This, was also confirmed by elemental analysis of the reaction mixture showing no presence of Re species, and subsequently validated by a filtration experiment, showing that the removal of the solid catalyst by filtration after 0.5 h of reaction stopped the DODH reaction advancement (Figure 2). These results, in combination with the data from the elemental analysis, also confirmed that the DODH reaction was not catalyzed homogeneously by solvated rhenium species but definitely by the heterogeneous ReO_x/Al_2O_3 catalyst.

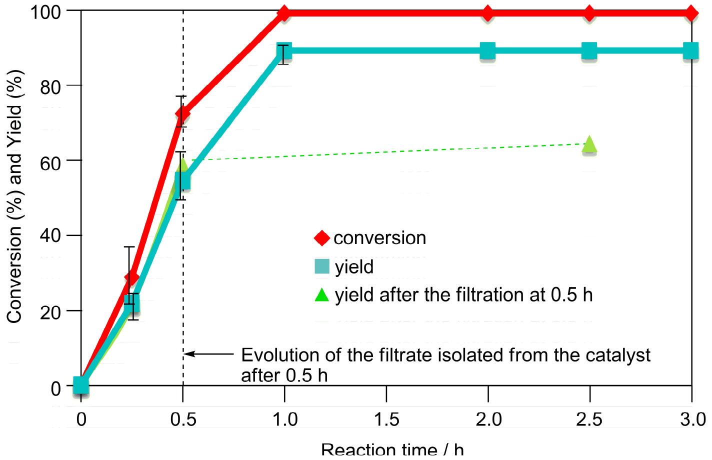

Figure 2. Glycerol conversion and allyl alcohol yield observed over the ReO_x/Al_2O_3 catalyst or in the absence of the solid catalyst as a function of time.

4. Conclusions

The DODH reaction of glycerol over a heterogeneous ReO_x/Al_2O_3 catalyst was successfully demonstrated yielding 92% in allyl alcohol. The catalyst was found reusable, which also demonstrated the heterogeneous nature of the reaction. With respect to the use of 2-octanol as sacrificial agent, the recycling of the latter was successfully demonstrated using commercial Ni based catalysts. The combination of both reactions allows to establish a fully integrated continuous process.

References

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