

Heterogeneous catalysis applied to the synthesis of glycerol derived solvents.

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Glycerol has been a well-known renewable chemical for centuries, but as a consequence of the increase of biodiesel production, in which glycerol appears as a concomitant product, an increasing interest has been raised in the research of new uses of glycerol, able to deal with the high volume availability of this product.

Glycerol can be used as commodity for the synthesis of a large number of interesting raw chemicals¹⁻³, but volatile market of glycerol is limiting some of those applications. An effort is needed in producing cheaper and easily available products from glycerol, as a renewable raw material, using heterogeneous catalysis in order to design greener processes.

One of the principles of green chemistry deals with the substitution of hazardous, toxic and volatile organic solvents (VOC's). In this sense, glycerol itself and some of its derivatives have been explored as green solvents⁴⁻⁶. The possibility of new uses of glycerol and its derivatives as solvent is highly attractive due to the ability to consume large amounts of this material.

In this context, the work presented herein focused on the development of green and efficient catalytic systems for the obtaining of glycerol derivatives, namely solketal and triacetin, with interesting properties as solvents.

Solketal has been widely used as solvent in several large-scale applications⁷⁻²⁰ such as in paint and ink formulations, cleaning products or in cooling agents. In the pharmaceutical industry, it has been used as additive for injectables, as vehicle for drugs in topical uses or in controlled delivery systems.

Triacetin has also been described as an effective solvent for many industrial application, such as caffeine extraction²¹.

We explore here the use of heterogeneous catalysts, such as montmorillonite K10 or sulfonated hydrothermal carbons (SHC), for the synthesis of solketal and triacetin. Commercial acid solids, such as Dowex 50W or Amberlyst 15 (with arylsulfonic groups) and Deloxan (with alkylsulfonic groups), will also be use for the sake of comparison.

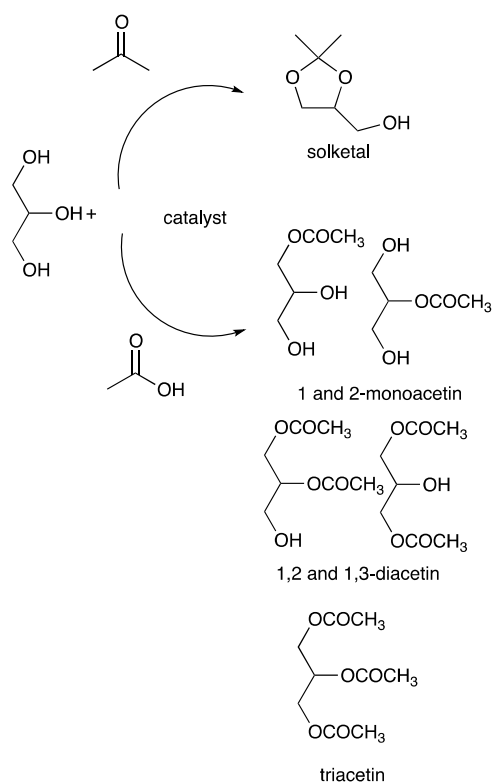


Fig. 1 – Synthesis of solketal and glycerol acetates from glycerol

The choice of SHC as catalyst for these reactions is based on the good activity displayed by this kind of solid in the esterification of fatty acids²². Moreover it is a material prepared from renewals (either glucose or other carbohydrates, such as sucrose or starch) under mild conditions.

In the case of solketal, when using homogeneous acid catalyst, such as H₂SO₄, good yields are achieved but elimination of the catalyst from the reaction media involves treatment with basic aqueous solutions, leading to a great loss of the desired ketal, up to 40%. Substitution of the homogeneous acid catalyst by heterogenous ones allowed not only the obtaining of high reaction yields but also an easy purification of the ketal by simply filtration. Dowex 50W, a sulfonic resin, together with K10 and SHC were tested in the reaction of glycerol with acetone at room

temperature. A molar excess of 5:1 of acetone was used and 1% wt catalyst. Figure 1 shows the results at 1 h and 4 h reaction time. SHC appears to be more active than K10 or Dowex for the solketal synthesis.

Above this, all the three catalyst were recovered with no loss of activity.

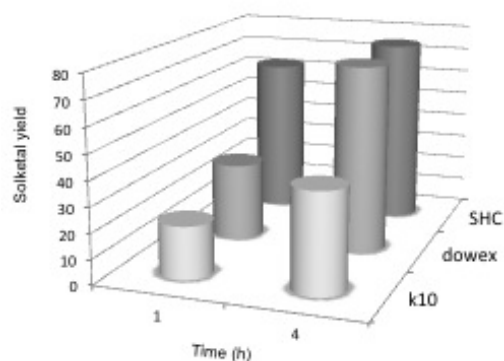


Fig. 2 – Results of the condensation of glycerol with acetone catalyzed by heterogeneous acid catalysts.

In the case of the synthesis of glycerol acetates, previous works demonstrated the difficulty of the obtaining of triacetin in high yields. Sulfonated heterogeneous catalysts, such as Amberlyst 15, had already been described as effective catalysts for this reaction^{23,24}. In fact, both Amberlyst and Deloxan show similar performance, with less than 50% yield of triacetin, in spite of the different acidity of their sulfonic groups. The use of sulfonated hydrothermal carbon as heterogeneous catalyst allowed 99% glycerol conversion in 0.5 h reaction time and the obtaining of mixtures of glycerol acetates with high contents of triacetin, up to 60%, and minimum amounts of monoacetin (<4%). Again SHC is the most effective catalyst described for the synthesis of triacetin from glycerol and acetic acid.

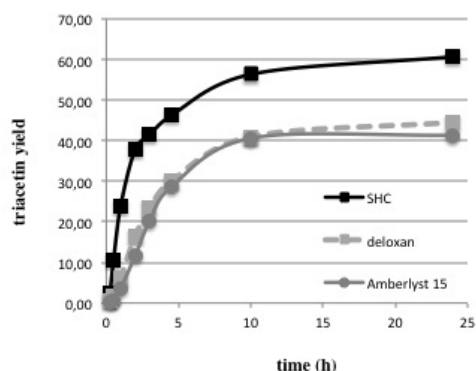


Fig. 3 – Triacetin yields in heterogeneous catalyzed reactions.

Further work is currently being done to optimize these results and to expand the applicability of this catalyst to other acid-catalyzed reactions.

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