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Bio-Glycidol Conversion to Solketal over Acid Heterogeneous Catalysts: Synthesis and Theoretical Approach

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Abstract: The present work deals with the novel use of heterogeneous catalysts for the preparation of solketal from bio-glycidol. Sustainable feedstocks and mild reaction conditions are considered to enhance the greenness of the proposed process. Nafion NR50 promotes the quantitative and selective acetalization of glycidol with acetone. DFT calculations demonstrate that the favored mechanism consists in the nucleophilic attack of acetone to glycidol concerted with the ring opening assisted by the acidic groups on the catalyst and in the following closure of the five member ring of the solketal.

Keywords: biomass; glycidol; heterogeneous catalysis; solketal

1. Introduction

Nowadays with the depletion of fossil fuels many efforts are devoted to the development of new green routes to convert renewables into biofuels [1,2]. This objective fully addresses the Green Chemistry principles proposed by Anastas and Warner in 1998 [3]. Among the others, the conversion of glycerol, mainly obtained as by product during biodiesel production, into value-added products is extremely important [4]. To this extent, several strategies have been investigated to convert glycerol into propanediols, dihydroxyacetone, allyl alcohol, polyglycerols, glycerol ethers, glycerol esters, etc. [5–9]. Among all the considered routes, the preparation of cyclic acetals and ketals through the reaction between glycerol and aldehydes/ketones in the presence of an acid catalyst represents one of the most promising alternatives [10,11]. In details, the condensation of glycerol with acetone yields a very interesting compound, namely solketal (2,2-dimethyl-1,3-dioxolane-4-methanol), employed as flavoring agent, surfactant and fuel additive. Herein water is produced as by-product and need to be removed to hinder the reversibility of the reaction. Solketal can be directly used to reduce biodiesel viscosity and to satisfy the established values for flash point and oxidation stability [12]. The most diffused approach for the synthesis of solketal starting from glycerol requires the use of large amounts of a strong homogeneous Bronsted acid catalyst. Recently, several papers reported on the use of heterogenous catalysts like Amberlyst resins, zeolites, montmorillonite K10, sulfonated silicas and silica-supported heteropolyacids. In 2012, Pescarmona and coworkers described the promising application of heterogeneous Lewis acid catalysts for the conversion of glycerol to solketal [13].

As alternative to glycerol, glycidol (2,3-epoxy-1-propanol) can be considered a potential candidate as starting molecule to synthesize solketal. However, the preparation of solketal starting from glycidol was barely investigated to date and always in the presence of homogeneous catalytic systems. More in detail, Iranpoor and Kazemi reported the conversion of glycidol to solketal (89% isolated yield after 2 h of reaction) in the presence of 0.2 molar equivalent of $RuCl_3$ in refluxing acetone [14]. Afterwards, the same research group reported good results also using 0.2 molar equivalent of iron(III)trifluoroacetate in refluxing acetone (89% as isolated yield after 4 h of reaction) [15]. More recently, Procopio et al. showed the quantitative conversion of glycidol to solketal in acetone at room temperature after 48 h in the presence of 1% in moles of $Er(OTf)_3$ [16]. The authors suggested a mechanistic scenario involving the oxirane ring activation through the coordination to the Er(III) followed by the nucleophilic attack of acetone.

The use of glycidol as starting material for solketal preparation becomes more interesting in the light of the recently investigated bio-based routes for its preparation. More in detail, we recently described the preparation of glycidol through the conversion of 2-chloro-1,3-propanediol (β-MCH), a by-product in the bio-based epichlorohydrin production plant [4,17,18]. This approach allows to valorize the entire production chain to bio-epichlorohydrin minimizing the production of waste in agreement with the twelve principles of Green Chemistry.

As a matter of fact, glycidol in turn can be easily used as starting material to produce high-value products through catalysis [19].

In this work, we report for the first time the selective preparation of solketal through glycidol ketalization with acetone in the presence of acid heterogeneous catalysts with the aim to increase the sustainability of this process.

The effect of temperature, glycidol/acetone ratio and catalyst loading has been investigated to find the optimal conditions for the reaction. Moreover, other ketones have been tested to prove the versatility of this approach and extend its generality. Finally, DFT calculations have been performed in order to rationalize the mechanism occurring.

2. Results and Discussion

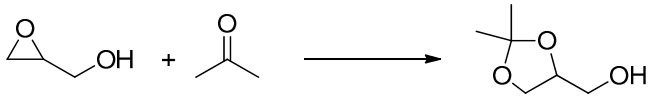
2.1. Glycidol Conversion to Solketal: Reaction Conditions Optimization

Initially, the tests were performed using a catalyst loading of 10 wt % with respect to glycidol and a glycidol/acetone molar ratio of 43, heating the system to reflux, as reported in literature for glycidol acetalization in homogeneous phase [20]. In these conditions, acetone acts both as reagent and reaction solvent, avoiding the need of any other organic solvent, finally simplifying the purification of the products and acetone recovery and recycle. This represent an important aspect for a potential industrial scale-up [21]. Herein, the preparation of solketal starting from glycidol permits us to easily separate the desired product at the end of the process using a rotary evaporator under reduced pressure thanks to the highly different boiling points of solketal (188 °C) and acetone (56 °C).

Several heterogeneous catalysts (both Lewis and Brønsted acids) have been used to promote glycidol acetalization to solketal. Nafion NR50, Montomorillonite K10 and Amberlyst-15 are commercially available whereas sulfonated charcoal, sufonated mesoporous silica and supported metal triflates have been prepared and successfully employed in acid-demanding processes [18]. As shown in Table 1, glycidol is successfully converted into the desired product using both Lewis and Brønsted heterogeneous acid catalysts. The best results in terms of conversion and selectivity to solketal are obtained in the presence of supported metal triflates (see entries 3–5) and Nafion NR50 (see entry 1). No reaction took place using Montmorillonite K10, sulfonated activated charcoal (AC-SO_3H) and sulfonated mesoporous silica (MS-SO_3H) (see Table S1) due to their known lower total acidity (0.21 mmol/g for Montmorillonite K10, 0.15 mmol/g for MPS-SO_3H and 0.18 mmol/g for AC-SO_3H) [18]. Amberlyst-15 (sulfonated styrene-divinyl benzene resin with a total acidity of 4.7 mmol/g) promotes the quantitative conversion of glycidol but a dramatic reduction of the

selectivity is observed due to a competitive glycidol oligomerization, as reported in our previous works for glycidol etherification with alcohols [18,22]. Among all the tested catalysts we evaluated the recyclability of Nafion NR50 and supported metal triflates in order to find the best catalytic system. Herein, in the presence of supported metal triflates no reaction took place due to active Lewis acid sites leaching. This phenomenon has been also recently reported in literature for $Al(OTf)_3$ on mesoporous silica-based catalysts during glycerol acetalization [23]. On the contrary, Nafion NR50 retains its high activity both in terms of conversion (90%) and selectivity to solketal (85%). It is worth to mention that the reported synthetic approach occurs with a 100% of atom economy with no formation of water. This aspect is crucial to avoid the undesirable deactivation of the sulfonic sites on Nafion NR50. The high activity of Nafion NR50 is related to Bronsted acidic sites and its perfluorinated polymeric structure as below confirmed by DFT calculations.

Table 1. Glycidol conversion to solketal in the presence of heterogeneous catalysts.



Experiment	Catalyst	Conversion (%)	Selectivity to Solketal (%)	Yield (%)
1	Nafion NR50	90	88	79
2	Amberlyst-15	100	8	8
3	$Bi(OTf)_3$ on MS	100	86	86
4	$Al(OTf)_3$ on MS	100	93	93
5	$Fe(OTf)_3$ on MS	100	87	87
6	No catalyst	0	-	-

Reaction conditions: glycidol/acetone moles ratio 1:43, t = 24 h, reflux, catalyst loading 10 wt %; MS: mesoporous silica.

With the best catalytic system, Nafion NR 50, we evaluated the effect of the temperature performing the reaction at room temperature. Herein, we observed only 24% conversion and 50% selectivity to solketal after 24 h due to the competitive glycidol oligomerization. As for the catalyst loading, reducing it from 10 wt % to 5 wt % only 58% of conversion with a total selectivity to solketal are achieved after 24 h. However, increasing the catalyst loading to 20 wt % allows to speed up the reaction and reach total conversion and selectivity to solketal. To evaluate the best acetone/glycidol ratio, catalytic runs were performed using a ratio of 20:1 under reflux for 18 h in the presence of 20 wt % of Nafion NR50. Results show a decrease of selectivity to solketal (80%) owing to glycidol oligomerization due to the more concentrated environment. Therefore, we continued our study by using the optimal conditions (acetone/glycidol molar ratio of 43, 20 wt % of Nafion NR50 and reflux conditions). The effect of the reaction time on conversion and selectivity under these optimized reaction conditions is shown in Figure 1. Nafion NR50 promotes the quantitative conversion (99%) of glycidol to solketal in 18 h with total selectivity to the desired product with a calculated TOF of 20 h^{-1}.

Moreover, the catalyst is stable under these reaction conditions and retains high efficiency during four consecutive cycles (see Figure S1 in Supplementary Materials). The recycled acetone has been characterized by GC-FID and analyses have demonstrated the high purity ensuring its potential reuse. This aspect is crucial at industrial level where the possibility to recycle the solvents increases the sustainability of the whole process with a drastic reduction of costs and environmental impacts [24].

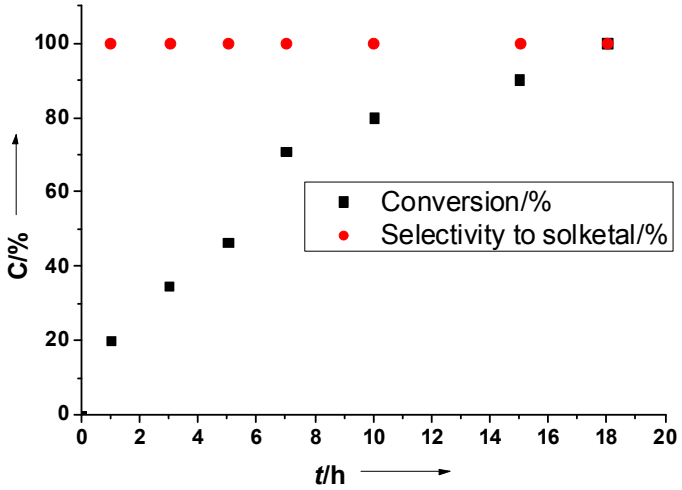
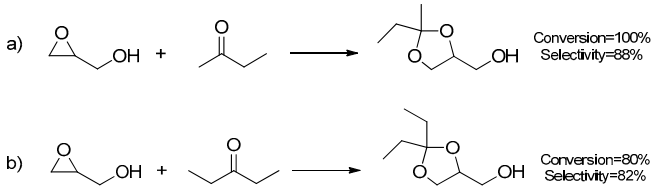


Figure 1. Glycidol conversion to solketal using Nafion NR50 (reaction conditions: glycidol/acetone moles ratio 1:43, catalyst loading 20 wt %, reflux).

Finally, in order to verify the generality of the studied reaction, we extended the substrate scope by using different ketones under the optimized reaction conditions (reflux, glycidol/ketone in moles ratio of 43, 18 h, 20 wt % of Nafion NR50). In details, methylethylketone (MEK) and 2-pentanone have been selected since the corresponding acetals can be opportunely used as building blocks to prepare high-value products such as monoalkyl glyceryl ethers [11]. Results are reported in Scheme 1. Glycidol is favorably converted into the corresponding acetals in both cases with high yields and selectivities, and glycidol oligomers are observed as by-products.



Scheme 1. Glycidol ketalization with ketones: methylethylketone (**a**), and 2-pentanone (**b**).

2.2. Theoretical Investigation of the Reaction Mechanism

The mechanism of the reaction between glycidol and acetone catalyzed by the best performing Nafion NR50 has been investigated by DFT calculations.

Two possible mechanistic scenarios have been investigated, see Figure 2. Pathway 1 implies the coordination of the epoxide to the catalyst trough formation of a hydrogen bond with the nucleophilic attack of the ketone that opens the ring in the following step; in pathway 2, instead, the catalyst activates acetone towards the nucleophilic addition of the -OH group on the glycidol and the epoxy ring opening occurs in the last step. The oxygen atom of the ketone moiety seems to be more nucleophile then the epoxy one, as proved by the almost 3 kcal/mol in favor of B′ adduct respect to B. Along pathway 1, after B formation, the ketone adds to the primary carbon atom of the epoxide with a concerted opening of the ring helped by the hydrogen transfer. The free energy barrier required is almost 24 kcal/mol. In C, the catalyst interacts with the substrate by formation of an oxygen-carbon bond that stabilizes the intermediate. The competing pathway with the ketone adding to the secondary carbon atom of the epoxide is both kinetically and thermodynamically unfavored by 1.4 and 5.8 kcal/mol, respectively. From C, the ex-epoxy oxygen adds to the ex-carbonyl carbon with the hydrogen returning to the sulfonate group on the catalyst and a barrier of almost 11.5 kcal/mol. Moving to pathway 2, the hydroxyl group of glycidol adds to the carbonyl carbon of acetone with a barrier of almost 21 kcal/mol.

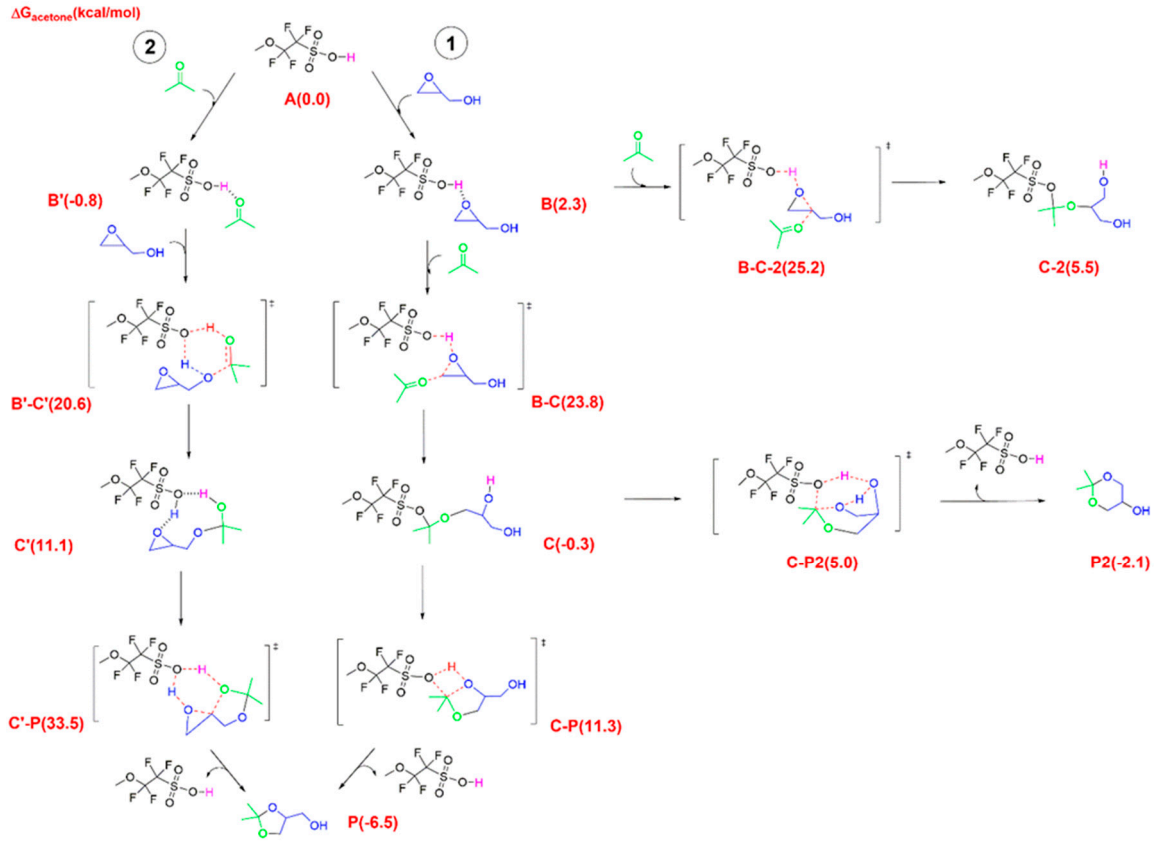


Figure 2. Mechanistic pathways investigated and corresponding free energies (kcal/mol in acetone).

The formation of the oxygen-carbon bond occurs simultaneously with two hydrogen transfers: the hydrogen of the sulphonic group transfers on the substrate and the hydrogen of the hydroxyl moiety transfers on the catalyst forming the intermediate C′ almost 10 kcal/mol lower than B′-C′. The following transition state C′-P consists in the opening of the epoxide ring concerted with the closure of the five member ring of the product P, 6.5 kcal/mol more stable than the starting reactants. This last step requires almost 34 kcal/mol ruling out this pathway, nevertheless the initial step is more favored along pathway 2 then along pathway 1. In conclusion, the favored mechanism consists in the ring opening of the epoxide by the nucleophilic attack of the ketone as rate determining step followed by an easier closure of the five member ring leading to the product. The formation of the corresponding six term ring product, P2 in Figure 2, is kinetically favored by almost 6 kcal/mol thanks to a most favorable geometry of the ring closing transition state. However, P2 is almost 5 kcal/mol less stable than P, that represents the thermodynamic product of the reaction, in agreement with the experimental findings (see Supplementary Materials). In order to rationalize the great performances showed by Nafion NR50 respect to the other heterogeneous systems tested, we have performed additional calculations for the reaction occurring in presence of sulfonated silica, as example of a not active catalyst for the considered reaction.

The favored pathway 1 of Figure 2 has been calculated for the catalytic system showed in Scheme S2 (see Supplementary Materials). The rate determining barrier for the nucleophilic attack of acetone to glycidol (B-C in in Figure S4) with the concerted ring opening assisted by the sulfonate moiety on the catalyst requires 28.1 kcal/mol for the silica system, i.e., almost 4.5 kcal/mol more than for the Nafion model. This result allows us to conclude that the great catalytic activity of Nafion is ascribed not only to the known higher concentration of acid groups on the catalyst respect to silicas for example, but also to the higher acidity of these groups that result to be more able to activate the glycidol towards the nucleophilic attack of the ketone, increasing meaningfully the yields of solketal formation.

3. Materials and Methods

3.1. Materials

Glycidol 96%, acetone, 3-pentanone, 2-butanone, Nafion NR 50 (0.7 mmol/g), Montomorillonite K10, activated charcoal, cetyltrimethylammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), $Bi(OTf)_3$, $Al(OTf)_3$, $Fe(OTf)_3$, Amberlyst-15 (acidity 4.7 mmol/g) and sulfuric acid were purchased from Sigma-Aldrich. Glycidol and acetone were distilled before experiments. Mesoporous silica (MPS), MPS-supported metal triflates ($Al(OTf)_3$, $Bi(OTf)_3$ and $Fe(OTf)_3$)), sulfonated activated charcoal and sulfonated MPS were synthesized and characterized as described in our previous publication [18].

3.2. Catalytic Conversion of Glycidol to Solketal: General Conditions

In these experiments, 350 µL of glycidol and 15.0 mL of acetone (1:43 moles ratio) were mixed together in a round bottom flask under magnetic stirring (300 rpm) for 24 h under reflux conditions in the presence of an appropriate amount of heterogeneous catalyst (glycidol/catalyst weight ratio of 10). Afterwards, heterogenous catalyst was removed by filtration, acetone was removed using a rotary evaporator and the reaction products were analysed by GC-FID.

3.3. Gas-Chromatographic (GC-FID) Analyses

GC-FID analyses were carried out by using a Thermo Trace GC equipped with a Famewax polar column (30 m × 0.32 mm i.d.). The initial oven temperature was 40 °C, then programmed to heat to 160 °C at 5 °C min^{-1}, then to 240 °C at 20 °C min^{-1} and held at 240 °C for 5 min with a flow rate of 1.0 $mLmin^{-1}$ (splitless injection mode was used). The injection volume was 1 µL. The FID temperature was 280 °C and 230 °C for the inlet. The integrated areas were converted into mole percentages for each component present in the sample by using calibration curves prepared for all the components and 3-ethoxy-1,2-propanediol as internal standard. The data obtained were used to calculate the conversion and selectivity of the reactant species. Conversion (C) and selectivity (S) to products were calculated as follows:

$$\text{Glycidol conversion } (\%) = \frac{(initial\ mol\ of\ glycidol - final\ mol\ of\ glycidol)}{initial\ mol\ of\ glycidol} * 100 \quad (1)$$

$$\text{Selectivity } (\%) = \frac{mol\ of\ defined\ product}{mol\ of\ reacted\ glycidol} * 100 \quad (2)$$

$$\text{Yield } (\%) = [\text{conversion } (\%) * \text{ selectivity } (\%)]/100 \quad (3)$$

The relative standard deviation of three replicates is lower than 4% in all cases.

4. Conclusions

In conclusion, we have reported the selective preparation of solketal through glycidol (obtained as value-added product from Epicerol process) acetalization with acetone in the presence of Nafion as heterogeneous catalyst. Notably, using a low catalyst loading of Nafion (1.5% in moles as SO_3H group toward glycidol) we demonstrated the quantitative conversion of glycidol to the desired product in 18 h of reaction under mild conditions (reflux, acetone/glycidol molar ratio of 43). Nafion is also stable allowing to be reused for several reaction cycles without any loss of activity and selectivity. The study has been also extended to other ketones and solketal derivates are produced under the optimized reaction conditions with good yields and selectivity. The use of a heterogeneous catalyst to perform this reaction represents the innovative part of this research together with the theoretical investigation of the reaction mechanism. In fact, the calculations performed allowed to discriminate the energetically favored mechanistic pathway, highlighting that the opening of the glycidol ring is likely to occur in the first step of the reaction, concerted with the nucleophilic attack of acetone to the

epoxy carbon. In fact, the alternative mechanism that sees the three member ring opening in the last step concerted with the solketal five member ring closure is almost 10 kcal/mol more energy requiring. Finally, the mechanistic pathway calculated for the system simulating the MS-SO_3H catalyst showed that the fluorinated polymeric skeleton of Nafion is more able to activate glycidol towards acetone addition decreasing the decisive reaction barrier.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/8/9/391/s1. Figure S1. Nafion NR50 recyclability. Figure S2. 1H-NMR (CDCl3, 400 MHz) spectrum of reaction mixture. Figure S3. 13C-NMR (CDCl3, 100 MHz) spectrum of reaction mixture. Figure S4. Mechanistic pathways investigated and corresponding free energies (kcal/mol in acetone) for the sulfonated-silica catalyzed reaction. Table S1. Glycidol conversion to solketal. Scheme S1. Nafion NR 50 modeled structure. Scheme S2. Sulfonated-silica modelled structure.

Author Contributions: M.R., L.F. and R.C. performed the experiments; R.C. and L.F. wrote the paper; F.C. and A.P. conceived and designed the experiments and discussed the results; T.T. supported the analysis of data and discussed the results.

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Conflicts of Interest: The authors declare no conflict of interest.

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