



Short communication

## Heterogeneous catalysis for the ketalisation of ethyl levulinate with 1,2-dodecanediol: Opening the way to a new class of bio-degradable surfactants



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### ABSTRACT

The acid-catalysed ketalisation between ethyl levulinate and two different alkyl 1,2-diols (ethylene glycol and 1,2-dodecanediol) was investigated using different acid catalysts, e.g. *p*-toluenesulfonic acid, Amberlyst 70, zeolite H-ZSM-5, and niobium phosphate. Good activity and recyclability were achieved in the reaction with ethylene glycol catalysed by niobium phosphate. Very promising results (both in diol conversion and in selectivity towards the desired ketal) were ascertained in the reaction with the longer-chain 1,2-dodecanediol catalysed by heterogeneous catalysts. The alkaline hydrolysis of the synthesised long-chain ketal ester allowed us to obtain a new green surfactant, with surface tension values falling in the range of the commercial anionic ones.

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### 1. Introduction

Many chemical products such as surfactants, plasticisers, and polymers are currently manufactured from non-renewable, expensive, petroleum-derived or natural gas-derived feedstock compounds. High raw material costs and uncertainty of future supplies impelled the discovery and development of chemical products that can be made from inexpensive renewable biomasses [1]. In this context, levulinic acid (or 4-oxopentanoic acid) (LA) and levulinic esters represent important platform molecules, obtained from biomass, which can be converted into valuable chemicals such as plasticisers, solvents, and flavours [2–10]. The reaction between levulinic acid esters and an alcohol leads to ketal formation and the presence of an acid catalyst is necessary. Diols, triols, and polyols can be also used to form cyclic ketals [11]. Acetalisation/ketalisation reactions are acid-catalysed processes. In the field of homogeneous catalysis, mineral acids are used. However, they present limitations due to corrosion, toxicity, and environmental pollution problems and need complex and expensive downstream steps, such as their neutralisation. On the other hand, heterogeneous catalysis presents easy work-up and does not involve the use of dangerous substances [12]. Many heterogeneous catalysts have been used in the acetalisation and ketalisation reactions, including zeolites, clays, sulfonic resins, mesoporous aluminosilicates, SBA-15, and niobium phosphate

[13–20]. During the acid-catalysed ketalisation reaction, the ketal ester or the keto-ester can undergo further competing transesterification with the alcohol [11], and therefore, some by-products can be obtained, decreasing the yield of the target valuable ketal ester. Mullen et al. [11] investigated the reaction between different keto-esters and diols/triols using a variety of catalyst types, catalyst concentrations, and reaction conditions. Different acids were tested, such as hydrochloric acid, sulphuric acid, sulfamic acid, and Amberlyst 15 and high conversion and selectivity to the ketal product were achieved by adopting a low concentration of the acid catalyst. Ono et al. [21] investigated the reaction of ethyl levulinate (EL) with various alkyl 1-O-alkyl glycerol, by using PTSA as catalyst and toluene as solvent. The authors reached variable yields in the range 78–98%. The ketal ester obtained was hydrolysed to produce an anionic surfactant. Ketal surfactants are in general more labile than the corresponding acetal surfactants [21,22]. Recently, the synthesis of sulfonated surfactants starting from furfural and carboxylate surfactants obtained from 5-HMF (5-hydroxymethyl furfural) is reported in the literature [23,24].

In the first part of this work, the study of the model reaction between ethyl levulinate (EL) and ethylene glycol (EG) will be reported, by using different acid catalysts, including Amberlyst 70 (A-70), zeolite H-ZSM-5, and niobium phosphate (NbP). *p*-toluenesulfonic acid (PTSA) will be considered as standard homogeneous acid catalyst for the ketalisation reaction, in order to better understand the improvement given by the heterogeneous catalysis. In this perspective, reaction between EL and EG will be studied adopting homogenous (PTSA) or heterogeneous

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(A-70, H-ZSM-5, and NbP) systems, starting from the worst reaction conditions at very low EL/EG molar ratio. Then, a deeper investigation of the reaction conditions will be tested, adopting different reaction conditions, such as catalyst loading, EL/EG molar ratio, and reaction time. Furthermore, the recyclability of the most promising heterogeneous catalysts will be studied.

Current research is focused on the use of longer-chain diol precursors, in order to improve the surface tension properties of the synthesised surfactants. In this sense, 1,2-dodecanediol may represent a good green solution, being currently used in cosmetics formulations [25]. Therefore, in the second part of this work, the acid-catalysed ketalisation reaction between the longer chain 1,2-dodecanediol and EL will be carried out, in the presence of homogeneous (PTSA) or heterogeneous (A-70 and NbP) catalysts. Surface tension of the sodium salt of the produced ketal will be evaluated, in order to verify their possible use as green surfactants.

## 2. Experimental

### 2.1. Materials

Commercial materials were used as received. Details about the procedures of treatment and properties of the catalysts A70, NbP, and H-ZSM-5 are described in the supplementary information.

### 2.2. Typical procedure of ketalisation reaction of ethyl levulinate with ethylene glycol and 1,2-dodecanediol

Catalytic liquid phase ketalisation reactions between ethyl levulinate and ethylene glycol or 1,2-dodecanediol were carried out as described in the supplementary information.

## 3. Results and discussion

### 3.1. Ketalisation reaction of ethyl levulinate with ethylene glycol

In the first part of this work, the model reaction between ethyl levulinate (EL) and ethylene glycol (EG) was considered in order to optimise the reaction conditions and identify the best catalysts, in terms of conversion and selectivity. The possible ketalisation/transesterification reactions are depicted in Fig. 1.

On the basis of Fig. 1, ethylene glycol could react with the ketone group, thus giving the target ketal product (2), or with the ester groups, thus producing a new ketal ester (3) or a new ester (4), both representing by-products. Niobium phosphate (NbP), sulfonic resin (A-70), and zeolite (H-ZSM-5) were tested as heterogeneous acid catalysts. These systems have been selected to avoid the drawbacks of homogeneous catalysts, such as waste generation, catalyst separation,

and neutralisation [26]. However, PTSA was also tested as reference homogeneous catalyst in order to compare homogeneous versus heterogeneous systems. The ketalisation is an equilibrium reaction and therefore it is appropriate to use an organic solvent, such as toluene, in order to remove the evolved water, thus increasing the yield in the desired ketal. The reaction was performed at 110 °C, by adopting different EL/EG molar ratios, equal to 0.5, 1.2, and 2.5. Because the choice of an EL excess could represent an economic limit, the lowest EL/EG molar ratio should be preferred. The results obtained by using EL/EG molar ratio = 0.5 are reported in Table 1 both for homogeneous (PTSA) and heterogeneous (A-70, H-ZSM-5, and NbP) catalytic systems.

This run shows that despite the acceptable catalytic activity of PTSA, the selectivity towards the desired ketalisation product (2) is very low, due to the formation of the by-product (3) and, in lower amount, of the by-product (4). On the contrary, all the investigated heterogeneous systems gave the almost complete selectivity towards the desired ketalisation product (2) (runs 2–8). On the other hand, the not complete conversion was probably due to the too low EL/EG molar ratio. The comparison among the catalytic performances obtained with heterogeneous catalysts immediately evidences that EL conversion was higher for the A-70-catalysed reactions (runs 2–4) rather than for the NbP- and H-ZSM-5-catalysed ones (runs 5–8). When A70 and H-ZSM-5 were employed (runs 2–4 and 7–8, respectively), selectivity towards the ketal product (2) was never complete, due to the formation of by-product (3). Instead, NbP evidenced a lower activity in EL conversion, but the selectivity to the target product (2) was complete (runs 5–6). Mullen et al. [11] evaluated the effect of H<sub>2</sub>SO<sub>4</sub> catalyst concentration in the ketalisation reaction between EL and EG. The authors reported a higher selectivity towards the product (2) when a lower catalyst concentration was used. In our case, the lower concentration of NbP acidic sites may justify the complete selectivity of the ketalisation reaction towards the product (2). The results of the ketalisation reaction between ethyl levulinate (EL) and ethylene glycol (EG) at higher EL/EG molar ratios adopting different catalytic systems PTSA, A-70, H-ZSM-5, and NbP are reported in Table 2.

When harsher reaction conditions were employed, in terms of catalyst loading and time (10 wt% and 24 h), all catalysts gave an incomplete selectivity towards the target product (2) (runs 9, 10, 14, and 18 for PTSA, A70, H-ZSM-5, and NbP, respectively, Table 2). By decreasing the catalyst loading from 10 to 1 wt% but increasing the EL/EG molar ratio from 1.2 to 2.5, it was possible to significantly reduce the reaction time, achieving a complete selectivity towards the ketalisation product (2) (runs 11, 15, and 19 for A70, H-ZSM-5, and NbP, respectively, Table 2). Taking into account the interesting result regarding the complete selectivity, the catalyst loading was further decreased from 1 to 0.1 wt% in order to find more sustainable reaction conditions. The catalytic runs carried out in the presence of the most active catalysts A70 and H-ZSM-5 (runs 12 and 16, respectively, Table 2) showed that the

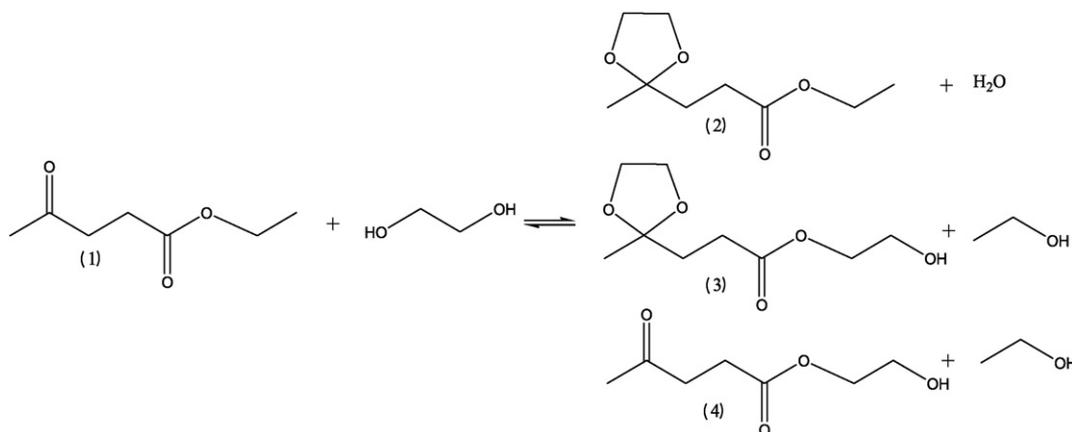


Fig. 1. Ketalisation reaction between ethyl levulinate (EL) and ethylene glycol (EG).

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