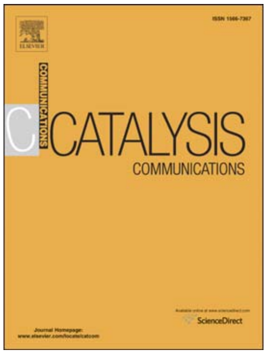


Heterogeneous catalysis for the ketalization of ethyl levulinate with 1,2-dodecanediol: Opening the way to a new class of bio-degradable surfactants

Flávio A. Freitas, Domenico Licursi, Elizabeth R. Lachter, Anna Maria Raspolli Galletti, Claudia Antonetti, Thamires C. Brito, Regina Sandra V. Nascimento

PII: S1566-7367(15)30106-0
DOI: doi: 10.1016/j.catcom.2015.10.011
Reference: CATCOM 4469

To appear in: *Catalysis Communications*

Received date: 13 August 2015
Revised date: 1 October 2015
Accepted date: 5 October 2015

Please cite this article as: Flávio A. Freitas, Domenico Licursi, Elizabeth R. Lachter, Anna Maria Raspolli Galletti, Claudia Antonetti, Thamires C. Brito, Regina Sandra V. Nascimento, Heterogeneous catalysis for the ketalization of ethyl levulinate with 1,2-dodecanediol: Opening the way to a new class of bio-degradable surfactants, *Catalysis Communications* (2015), doi: 10.1016/j.catcom.2015.10.011

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

Flávio A. Freitas [a], Domenico Licursi [b], Elizabeth R. Lachter*[a], Anna Maria Raspolli Galletti [b], Claudia Antonetti [b], Thamires C. Brito [a] and Regina Sandra V. Nascimento [a]

[a] *Universidade Federal do Rio de Janeiro, Instituto de Química, Rio de Janeiro, Brazil.*

[b] *Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124, Pisa, Italy.*

** Corresponding author. E-mail address: lachter@iq.ufrj.br*

The acid-catalysed ketalization 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*-toluensolfonic acid, Amberlyst 70, zeolite H-ZSM-5 and niobium phosphate. Good activity and recyclability were achieved in the reaction with ethylene glycol catalyzed 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 catalyzed by heterogeneous catalysts. The alkaline hydrolysis of the synthetized 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.

Keywords: ethyl levulinate, ketalization, heterogeneous catalysis, niobium phosphate

1. Introduction

Many chemical products such as surfactants, plasticizers, 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 plasticizers, 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]. Acetalization/ketalization reactions are acid-catalyzed 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 neutralization. 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 acetalization and ketalization reactions, including zeolites, clays, sulfonic resins, mesoporous aluminosilicates, SBA-15 and niobium phosphate [13-20]. During the acid-catalyzed ketalization 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*-toluensolfonic acid (PTSA) will be considered as standard homogeneous acid catalyst for the ketalization 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 (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 synthetized 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 ketalization 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 ketalization reaction of ethyl levulinate with ethylene glycol and 1,2-dodecanediol

Catalytic liquid phase ketalization 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. Ketalization 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 optimize the reaction conditions and identify the best catalysts, in terms of conversion and selectivity. The possible ketalization/transesterification reactions are depicted in Fig. 1.

Figure 1, near here

On the basis of the 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 because avoid the drawbacks of homogeneous catalysts, such as waste generation, catalyst separation and neutralization [26]. However, PTSA was also tested as reference homogeneous catalyst in order to compare homogeneous versus heterogeneous systems. The ketalization 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.

Table 1, near here

This run shows that, despite the acceptable catalytic activity of PTSA, the selectivity towards the desired ketalization 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 ketalization 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_2SO_4 catalyst concentration in the ketalization 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 ketalization reaction towards the product (2). The results of the ketalization 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.

Table 2, near here

When harsher reaction conditions were employed, in terms of catalyst loading and time (10 wt % and 24 h), all catalysts gave an incomplete selectivity toward 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 ketalization 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 complete selectivity towards the target product (2) was retained at the same low reaction time (1h), despite of the EG conversion decrease. On the basis of these results, in order to improve the EG conversion, a longer reaction time (4h) was employed for all the heterogeneous catalysts (runs 13, 17 and 21 for A70, H-ZSM-5, NbP respectively, Table 2). Remarkable catalytic results were achieved with all the catalytic systems due to the almost complete conversion together with the total selectivity towards the ketalization product (2). The most promising catalytic results were obtained with zeolite H-ZSM-5 and thus this system was further investigated for its recyclability. Anyway, the recycle of this catalyst was not satisfactory, showing a decrease of its catalytic activity of about 30 % in the first recycle, probably due to the inefficient mild adopted catalyst regeneration procedure carried out simply by toluene washing.

On the other hand, NbP is well-known as a water-tolerant catalyst [27]. The acidic, textural, and catalytic properties of NbP are preserved in aqueous systems under harsher reaction conditions of temperature [28, 29] than those employed in the current research. Moreover, niobium is the 33rd most abundant element in the Earth's crust, so it is a plentiful resource and at the same time it is also nontoxic and physiologically inert [30]. Therefore, it was selected for the subsequent recyclability investigation. Five recycling tests were carried out on NbP. After each catalytic run, also in this case, the catalyst was simply washed with toluene and reused. After five cycles, catalyst has retained a high activity and selectivity to the desired ketal, as shown in Fig. 2.

Figure 2, near here

The above catalytic runs show that NbP recycle has not significantly modified its acidic properties, and the ascertained surface area of the recovered catalyst remained almost unchanged (120 m^2 g^{-1} versus 138 m^2 g^{-1}), thus confirming that our heterogeneous catalysis approach can be applied to the eco-friendly synthesis of these ketals.

3.2. Ketalization reaction of ethyl levulinate with 1,2-dodecanediol

After having investigated the chemical behaviour of EL and EG towards ketalization by means of heterogeneous catalysis, new ketalization reactions were performed by using a more long-chain vicinal diol, that is 1,2-dodecanediol, in order to evaluate the possibility of synthesizing a new class of efficient bio-surfactants.

Also in this case, an EL excess was adopted, e.g. a molar ratio EL/1,2-dodecanediol = 2.5, with PTSA, A-70, NbP and H-ZSM-5 as acid catalysts. Many different reaction conditions were tested and it was found that, differently from ethylene glycol, the high conversion of 1,2-dodecanediol has required a longer reaction time, that is 24 hours, by adopting the lowest catalyst loading. Best-obtained results are reported in Table 3.

Table 3, near here

When PTSA, A70 and NbP catalysts were employed (runs 22-24, respectively), selectivities towards ketalization product (2) were complete and therefore no transesterification by-products were obtained, as confirmed by ^{13}C-NMR and HPLC analysis of the reaction mixture. Only in the case of the homogeneous PTSA it is possible to reach the total 1,2-dodecanediol conversion, whereas for the other heterogeneous systems (A70 and NbP), promising values about 80-85 % were ascertained. On the other hand, when the reaction was carried out in the presence of H-ZSM-5, the selectivity towards the target product (2) was slightly lower than that of the other heterogeneous systems, under the same reaction conditions. On the basis of these results, ketal ester coming from A-70 and NbP catalyzed reactions was selected for its further purification, due to the incomplete conversion of the diol. Then, the obtained ketals were hydrolysed by NaOH/EtOH treatment and surface tensions of all the synthesized sodium carboxylate surfactants were analogous. The surface tension of H_2O is 72.2 mN m^{-1} and in the presence of the new surfactant this value decreases to 33.5 mN m^{-1} (supplementary information).

4. Conclusions

In this investigation, a green bio-surfactant was prepared by using renewable and cheap reagents. Heterogeneous catalysts, Amberlyst A70, zeolite H-ZSM-5 and niobium phosphate, were tested in the model ketalization reaction between ethyl levulinate and ethylene glycol. In fact, high yields and selectivities towards the target ketalization product were ascertained. On the contrary, when the homogeneous PTSA system was adopted, a big amount of by-products was obtained. In the presence of heterogeneous systems, the results were improved by the optimization of the main reaction parameters, catalyst loading, EL/EG molar ratio and reaction time. NbP resulted a very promising system, due to its complete recyclability and good performances also at low catalyst loading, taking also into account that, up to now, this catalytic system has not been proposed for the ketalization reaction. A new kind of bio-surfactant was synthesized starting from ethyl levulinate and 1,2-dodecanediol, in the presence of the same heterogeneous catalysts. The surface tension of this bio-derivative was similar to that of the commercial sodium dodecyl sulphate (SDS) surfactant.

Acknowledgements

F.A. Freitas wishes to acknowledge Conselho de Aperfeiçoamento de Ensino Superior – CAPES of Brazil for a Doctoral Grant. The authors thank Dr. Bianca Peres Pinto for the GC-MS analysis. The authors also thank CBMM (Companhia Brasileira de Metalurgia e Mineação) and Rhom & Haas for kindly providing niobium phosphate and Amberlyst 70, respectively.

References

[1] A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411-2502.

[2] A. Mukherjee, M.J. Dumont, V. Raghavan, Biomass Bioenerg. 72 (2015) 143-183.

[3] A.M. Raspolli Galletti, C. Antonetti, V. De Luise, M. Martinelli, Green Chem. 14 (2012) 688-694.

[4] I. Allaoua, B.E. Goi, M.M. Obadia, A. Debuigne, C. Detrembleur, E. Drockenmuller Polym. Chem. 5 (2014) 2973-2979.

[5] M.J. Climent, A. Corma, S. Iborra, Green Chem. 16 (2014) 516-547.

[6] A.M. Raspolli Galletti, C. Antonetti, E. Ribechini, M.P. Colombini, N. Nassi, E. Bonari, Appl. Energ. 102 (2013) 157-162.

[7] A.M. Raspolli Galletti, C. Antonetti, V. De Luise, D. Licursi, N. Nassi, BioResources 7 (2012) 1824-1835.

[8] P. Gallezot, Chem. Soc. Rev. 41 (2012) 1538-1558.

[9] D.W. Rackemann, W.O.S. Doherthy, Biofuels, Bioprod. Biorefin. 5 (2011) 115-126.

[10] E.S. Olson, M.R. Kjelden, A.J. Schlag, R.K. Sharma, ACS Sym. Ser. 784 (2001) 51-63.

[11] B.D. Mullen, V. Badarinarayana, M. Santos-Martinez, S. Selifonov, Top. Catal. 53 (2010) 1235-1240.

[12] R. Ballini, G. Bosica, B. Frullanti, M. Raimondo, G. Giovanni, S. Sartori, F. Schroer, Tetrahedron Lett. 39 (1998) 1615-1618.

[13] G.D. Yadav, S.O. Katole, Catal. Today 237 (2014) 125-135.

[14] V. Calvino-Casilde, K. Stawicka, M. Trejda, M. Ziolek, M.A. Banares, J. Phys. Chem. C 118 (2014) 10780-10791.

[15] C.X.A. da Silva, V.L.C. Gonçalves, C.J.A. Mota, Green Chem. 11 (2009) 38-41.

[16] E. Pérez-Mayoral, R.M. Martín-Aranda, A.J. López-Peinado, P. Ballesteros, A. Zukal, J. Cejka, Top. Catal. 52 (2009) 148-152.

[17] M.W.C. Robinson, A.E. Graham, Tetrahedron Lett. 48 (2007) 4727-4731.

[18] B. Thomas, S. Sugunan, J. Porous Mat. 13 (2006) 99-106.

[19] S.M. Mahajani, A.K. Kolah, M.M. Sharma, React. Funct. Polym. 28 (1995) 29-38.

[20] A.O. Barros, A.T. Faísca, E.R. Lachter, R.S.V. Nascimento, R.A.S. San Gil, J. Braz. Chem. Soc. 22 (2011) 359-363.

[21] D. Ono, A. Masuyama, Y. Nakatsuji, M. Okahara, S. Yamamura, T. Takeda, J. Am. Oil Chem. Soc. 70 (1993) 29-36.

[22] T. Kida, N. Morishima, A. Masuyama, Y. Nakatsuji, J. Am. Oil Chem. Soc. 71 (1994) 705-710.

[23] K.S. Arias, M.J. Climent, A. Corma, S. Iborra, ChemSusChem 7 (2014) 210-220.

[24] A. Gassama, C. Ernenwein, A. Youssef, M. Agach, E. Riguet, S. Marinković, B. Estrine, N. Hoffmann, Green Chem. 15 (2013) 1558-1566.

[25] W. Johnson Jr., W.F. Bergfeld, D.V. Belsito, R.A. Hill, C.D. Klaassen, D. Liebler, J.G. Marks Jr., R.C. Shank, T.J. Slaga, P.W. Snyder, F.A. Andersen, Int. J. Toxicol. 31 (2012) 147-168.

[26] J.H. Clark, J.W. Comerford, D.J. Macquarrie, Green Catalytic Transformations, in: Innovations in Green Chemistry and Green Engineering, P.T. Anastas, J.B. Zimmerman, (Eds.), Springer Science, New York, USA, 2013, pp. 37-80.

[27] Y. Zhang, J. Wang, X. Li, X. Liu, Y. Xia, B. Hu, G. Lu, Y. Wang, Fuel 139 (2015) 301-307.

[28] H. Gómez Bernal, L. Bernazzani, A.M. Raspolli Galletti, Green Chem. 16 (2014) 3734-3740.

[29] H. Gómez Bernal, A.M. Raspolli Galletti, G. Garbarino, G. Busca, E. Finocchio, Appl. Catal. A: Gen. 502 (2015) 388-398.

[30] V.S. Mallela, V. Ilankumaran, N.S. Rao, Indian Pacing Electrophysiol. J. 4 (2004) 201-212.

Table 1 Results of the ketalization reaction between ethyl levulinate (EL) and an excess of ethylene glycol (EG), in the presence of different heterogeneous acid catalysts. Reaction conditions: Catalyst loading = 3 wt%, EL/EG molar ratio = 0.5, Temperature = 110°C.

Run	**Catalyst**	**Time (h)**	**EL Conversion (mol%)**	**Selectivity to product (2) (mol%)**	**Selectivity to product (3) (mol%)**
1	PTSA	1	78	18	41 [a]
2	A70	0.5	58	94	6
3	A70	1	82	94	6
4	A70	4	87	96	4
5	NbP	1	50	100	-
6	NbP	4	54	100	-
7	H-ZSM-5	1	65	97	3
8	H-ZSM-5	4	68	96	4

[a] 7 mol % of product (4) together with other by-products were produced.

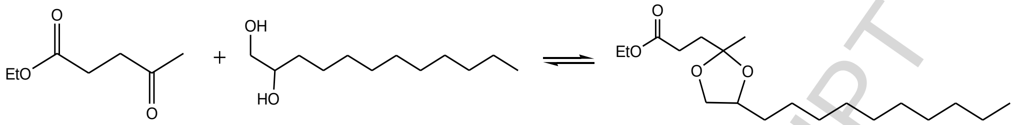
Table 2 Results of the ketalization reaction between ethyl levulinate (EL) and ethylene glycol (EG). Reaction conditions: Temperature = 110°C.

Run	**Catalyst**	**Catalyst loading (wt %)**	**EL/EG molar ratio**	**Time (h)**	**EG Conversion (mol %)**	**Selectivity to product (2) (mol %)**	**Selectivity to product (3) (mol %)**
9	PTSA	10	1.2	24	96	20.1	33 [a]
10	A70	10	1.2	24	100	86.3	6.6 [b]
11	A70	1	2.5	1	96.8	100	-
12	A70	0.1	2.5	1	85	100	-
13	A70	0.1	2.5	4	99	100	-
14	H-ZSM-5	10	1.2	24	100	90.2	9.8
15	H-ZSM-5	1	2.5	1	98	100	-
16	H-ZSM-5	0.1	2.5	1	85.5	100	-
17	H-ZSM-5	0.1	2.5	4	100	100	-
18	NbP	10	1.2	24	100	98.5	1.5
19	NbP	1	2.5	1	82	100	-
20	NbP	0.1	2.5	1	80.3	100	-
21	NbP	0.1	2.5	4	96	100	-

[a] 8.5 mol % of product (4) together with other by-products were produced.

[b] 3.9 mol % of product (4) together with other by-products were produced.

Table 3 Results of the ketalization reaction between ethyl levulinate (EL) and 1,2-dodecanediol, in excess of ethyl levulinate.



Run	Catalyst	1,2-dodecanediol Conversion (mol%)	Selectivity to product (2) (mol%)
22	PTSA	100	100
23	A70	85	100
24	NbP	81	100
25	H-ZSM-5	82	98

Reaction conditions: EL/1,2-dodecanediol = 2.5 mol/mol; catalyst loading = 1 wt %; reaction time = 24 hours; Temperature = 130 °C.

Captions for figures and schemes

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

Fig. 2. Catalytic performances (conversion and selectivity) of NbP to ketal, after five catalytic cycles (run 21 and successive recycles of the solid catalyst). Reaction conditions: Catalyst loading = 0.1 wt%, EL/EG molar ratio = 2.5, reaction time = 4 hours, Temperature = 110°C.

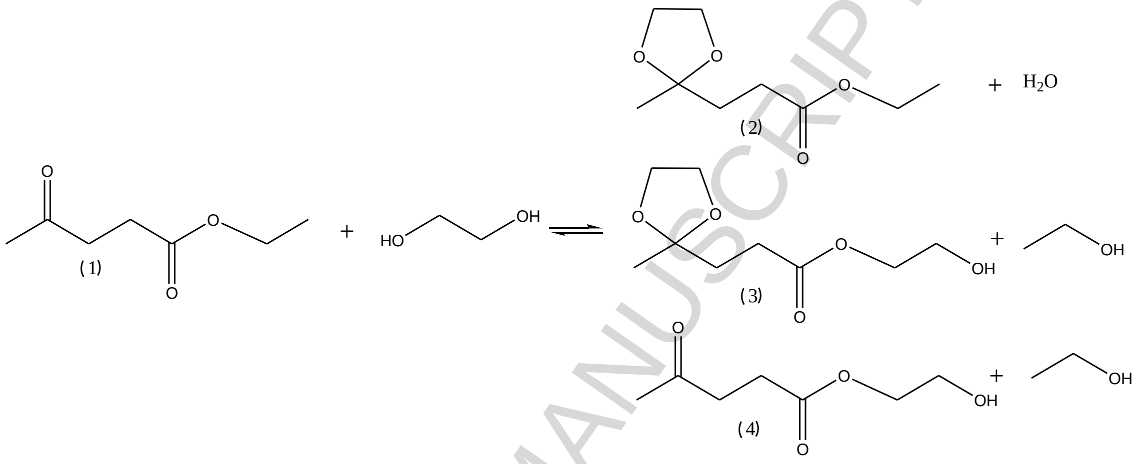


Fig. 1. Ketalization reaction between ethyl levulinate (EL) and ethylene glycol (EG).

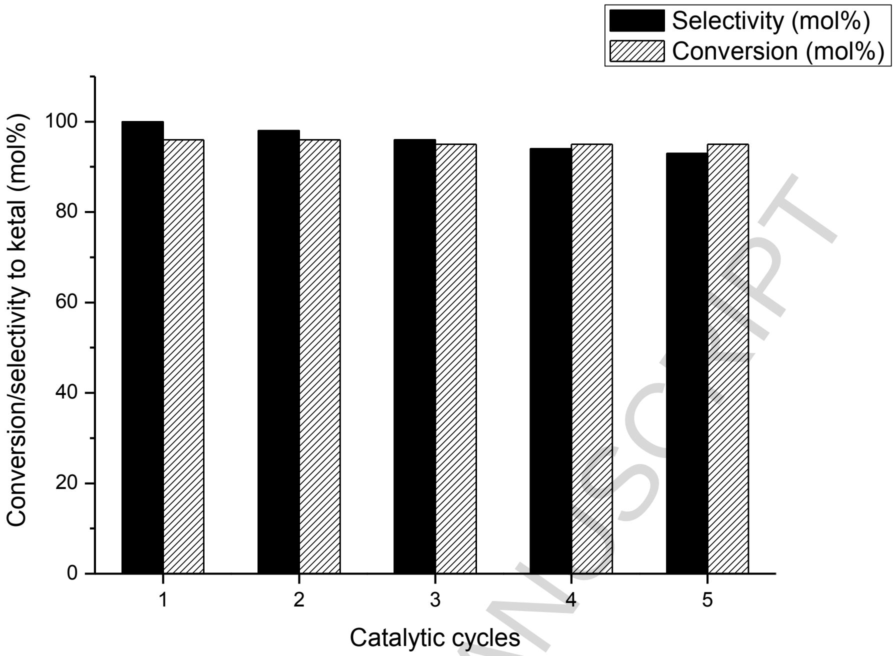


Fig. 2. Catalytic performances (conversion and selectivity) of NbP to ketal, after five catalytic cycles (run 21 and successive recycles of the solid catalyst). Reaction conditions: Catalyst loading = 0.1 wt%, EL/EG molar ratio = 2.5, reaction time = 4 hours, Temperature = 110°C.

Highligths

- Ketalization reaction between ethyl levulinate and alkyl 1,2-diols was evaluated.
- Different heterogeneous catalysts have showed good catalytic performances.
- Niobium phosphate was preferred for its easier and better recyclability.
- A surfactant was synthetized by alkaline hydrolysis of the ketal with longer chain.
- The new green bio-surfactant showing good surface tension properties.