Catalysis Communications 124 (2019) 6–11

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Solid acid catalyzed aldol dimerization of levulinic acid for the preparation of C10 renewable fuel and chemical feedstocks

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ARTICLE INFO

Keywords:
Levulinic acid
Aldol condensation
Solid acid
Silica - sulfuric acid
Dimerization

ABSTRACT

The acid catalyzed condensation of levulinic acid was studied using a series of solid acid catalysts: Amberlyst-15, SiO_2-SO_3H, Dowex50WX8, Carbon-SO_3H, TiO_2-SO_3H, Al_2O_3-SO_3H, $H_3PW_{12}O_{40}$, and $Nb_2O_5.H_2O$ under neat conditions at 110–130 °C. The major dimerization product was identified as tetrahydro-2-methyl-5,γ-dioxo-2-furanpentanoic acid. In addition, four minor products were identified as diastereomeric pairs of 3-(2-methyl-5-oxo-tetrahydrofuran-2-yl)-4-oxopentanoic acid and 3-acetyl-2-methyl-tetrahydro-5-oxo-2-furanpropanoic acid by spectroscopic and computational methods. A mechanism is proposed to explain the formation of five dimerization products where the major product is formed via the aldol condensation of C5 enol form of levulinic acid and four minor products are arising from the aldol condensations C3 enol form of levulinic acid. The highest total yield 56% was obtained with the use SiO_2-SO_3H as the solid acid catalyst and the reminder of the mass balance was unreacted levulinic acid. The SiO_2-SO_3H catalyst could be recycled four times with some loss in catalytic activity.

1. Introduction

Cellulose is the major structural component in green plants and many forms of algae. The resourceful utilization of this abundant carbohydrate polymer is a major challenge in achieving a renewable carbon based economy. The structural complexity of plant matter due to hydrogen bonding and close packing with lignin gives the recalcitrance to the cellulosic plant materials. However dilute aqueous acid catalysts at high temperature and pressure can be used in depolymerization of cellulose and further transformations of the sugars to produce industrially useful feedstock chemicals [1]. The monosaccharides produced in cellulosic biomass hydrolysis can undergo dehydration to 5-hydroxymethylfuran under acid catalysis conditions. Then rehydration of this C6 furan in aqueous acidic medium can lead to the more stable C5 keto-acid, commonly known as levulinic acid (LA) with the loss of one carbon as formic acid [2,3]. Galletti and co workers have recently studied the hydrothermal conversion of biomass materials: poplar saw dust, olive tree pruning and wheat straw to levulinic acid using dilute aqueous hydrochloric acid catalyst at 180–200 °C [4]. In these experiments they have obtained levulinic acid in 12–29% range yields based on the weight of raw materials, depending on the acid concentration, temperature and the reaction time [4]. Levulinic acid is a versatile renewable feedstock chemical that can be used in the preparation of a wide range polymer as well as fuel precursors and upgrading of this keto-acid is a current research interest [5–7].

Since 2013, a few research groups have studied the dimerization of levulinic acid as a way of upgrading the small C5 keto-acid to a more useful C10 feedstock. In a recent study Ordonez has shown that Mg—Zr mixed oxide catalyzed reaction of levulinic acid in aqueous medium at 323 K gives a mixture of three products. These products were identified as: α-angelica lactone and two aldol condensation adducts, levulinic acid dimer and levulinic acid - α-angelica lactone condensation product [8]. The use of NiMo/Al_2O_3 as the catalyst and hydrogen under neat conditions a levulinic acid dimerization resulted the decarboxylated product 1-oxo-6-methylspiro[4,4]nonan-2-one [9]. In a base catalyzed example of self dimerization of levulinic acid ethyl ester using sodium ethoxide as the base catalyst, a tetrasubstituted cyclopentadiene was found as the principal product [10]. The electrochemical coupling of levulinic acid is another approach that has attracted recent attention where octane-2,7-dione was formed as a result of decarboxylation and radical coupling [11]. In another recent study, Li and co-workers used a catalytic system containing $ZnCl_2$ and trichloacetic acid and showed

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https://doi.org/10.1016/j.catcom.2019.02.022
Received 12 February 2019; Accepted 22 February 2019

that the combination of Lewis and Brønsted acid is required for the dimerization of levulinic acid to give two C10 compounds [12].

We have been working on catalytic upgrading of renewable feedstocks for over a decade and our recent efforts have opened new routes for upgrading levulinic acid, including a new route for the preparation of a renewable C7 polymer building block by aldol condensation between LA and glyoxylic acid [13–15]. During this work we reported the facile preparation of the *bis*-lactone, 1-methyl-2,8-dioxabicyclo[3.3.0]oct-4-ene-3,7-dione by sulfuric acid catalyzed condensation of LA with glyoxylic acid at 80 °C, without a solvent, and the resulting unsaturated lactone could be catalytically reduced to a well-known polymer building block [13]. In another study we reported sulfuric acid and Amberlyst-H^+ catalyzed condensations of levulinic acid with paraformaldehyde under neat conditions at 80 °C gives 2,9,11,14-tetraoxadispiro[4.1.5.3]pentadecane-3,6-dione in 91–93% yield [16]. In our efforts on upgrading the levulinic acid by base catalyzed aldol reaction, we have found that NaOH catalyzed aldol condensation reaction between 5-hydroxymethylfurfural and levulinic acid in water gives a 2.5:1 mixture of aldol products: *(E)*-6-[5-(hydroxymethyl)furan-2-yl]-hex-4-oxo-5-enoic acid and (*E*)-3-[5-(hydroxymethyl)furan-2-yl]methylene-4-oxo-pentanoic acid in 82% combined yield. A similar reaction between furfural and levulinic acid gives the linear polymer, *poly*[1-carboxymethyl-4-(furan-2-yl)-2-oxo-butane-1,4-diyl] in 91% yield [17]. In continuation of our efforts we have found that solid acid catalyzed self aldol condensation reactions of levulinic acid gives mixture of aldol dimers as shown in Fig. 1. In this publication we describe the screening of a series of eight solid acid catalysts, identification of levulinic acid aldol condensation products and the possibility of reusing the solid acid catalyst in the dimerization reaction.

2. Experimental

2.1. Materials and instrumentation

Levulinic acid (> 99%), Amberlyst-15, Dowex50WX8, $H_3PW_{12}O_{40}$, $Nb_2O_5.H_2O$ and Diazald [*N*-methyl-*N*-(*p*-tolylsulfonyl) nitrosamide] were purchased from Aldrich Chemical Co. The solid acid catalysts carbon-SO_3H [18], SiO_2-SO_3H [19], TiO_2-SO_3H [20] and Al_2O_3-SO_3H [21] were prepared by standard literature procedures and gave physical properties comparable to the reported values. The $[H^+]$ density of these catalysts was determined by titration with standard 0.05 M aq. NaOH using phenolphthalein as the indicator. The acid $[H^+]$ density values of catalysts are shown in Table 1. ^1H NMR spectra were recorded in $CDCl_3$ on a Varian Mercury plus spectrometer operating at 400 MHz and chemical shifts are given in ppm downfield from TMS ($\delta = 0.00$). ^{13}C NMR spectra in $CDCl_3$ were recorded on the same spectrometer operating at 100 MHz; chemical shifts were measured relative to $CDCl_3$ and converted to δ(TMS) using $\delta(CDCl_3) = 77.00$. The methyl ester products were analyzed using a Varian 3900/Saturn 2100 T GC/MS system; carrier gas flow rate 1.0 mL min^{-1}, split ratio 1:20, injector temperature of 180 °C, with Saturn GC/MS WS Ver. 5.5 Software.

Scanning Electron Microscopy was performed using a JEOL JSM-6010LA using InTouchScope software. The backscattered electron images was collected using an accelerating voltage of 10 kV and a load current ~90 μA with a working distance of 9 mm. at a magnification of 1000 × and the analyzed area was 0.15 mm^2 (110 μm × 135 μm).

2.2. General procedure for the solid acid catalyzed dimerization of levulinic acid

A mixture of levulinic acid (116 mg, 1.0 mmol), solid acid catalyst (10–20 mol%) was prepared in a small glass vial, closed tightly and heated in an oil bath at 110–130 °C for 6–12 h. The resulting mixture was diluted with 20 mL of *t*-butyl methyl ether, centrifuged at 1700*g* for 5 min to remove the catalyst. The ether layer was concentrated and analyzed using NMR to determine the product composition. The catalyst used, reaction conditions, yields, and product ratios in solid acid catalyzed aldol dimerization of levulinic acid are shown in Table 1. A representative ^1H NMR spectrum of the product from entry 4 in Table 1 is shown in Fig. 2.

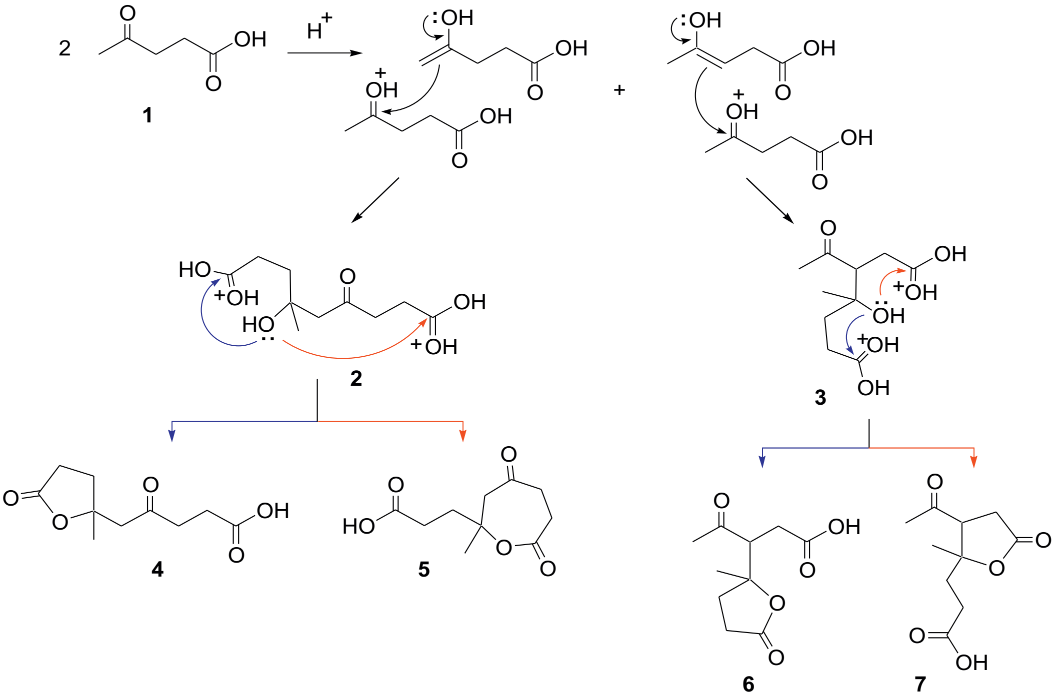


Fig. 1. The possible reaction paths for solid acid catalyzed aldol dimerization of levulinic acid (**1**) to give C10 compounds (**4–7**). The major product **4** and diastereomeric pairs of **6** and **7** are observed in the product mixture. Product **5** was not observed.

Table 1
The catalyst used, reaction conditions, yields, and product ratios in solid acid catalyzed aldol dimerization of levulinic acid. 1.0 mmol of levulinic acid was used in all experiments.

Entry	Catalyst	$[H^+]$ Density mmol/g	Catalyst loading (mol %)	Reaction condition	LA Conversion (%)	% Yield (4 + 5 + 7)	Product ratio 4:(5 + 7)
1	Amberlyst-15	4.7	5	110 °C, 6 h	40	38	58:42
2	Amberlyst-15	4.7	10	130 °C, 6 h	45	43	58:42
3	SiO_2-SO_3H	5.2	5	110 °C, 6 h	40	35	65:35
4	SiO_2-SO_3H	5.2	10	130 °C, 6 h	60	56	66:34
5	SiO_2-SO_3H	5.2	10	130 °C, 12 h	56	54	66:34
6	SiO_2-SO_3H	5.2	20	130 °C, 6 h	61	52	65:35
7	SiO_2-SO_3H	5.2	10	120 °C, 6 h	50	45	62:38
8	SiO_2-SO_3H	5.2	10	120 °C, 12 h	50	47	66:34
9	SiO_2-SO_3H	5.2	10	140 °C, 6 h	49	39	60:40
10	Dowex 50WX8	1.7	10	130 °C, 6 h	45	37	62:38
11	Carbon-SO_3H	1.1	10	130 °C, 6 h	20	15	64:36
12	TiO_2-SO_3H	1.0	10	130 °C, 6 h	2	2	38:62
13	Al_2O_3-SO_3H	3.6	10	130 °C, 6 h	2	2	100:0
14	$H_3PW_{12}O_{40}$	1.0	10	130 °C, 6 h	42	32	44:56
15	Nb_2O_5. H_2O	3.8	10	130 °C, 6 h	0	0	–

2.3. Preparation of methyl esters of levulinic acid dimerization products

A mixture of levulinic acid (116 mg, 1.0 mmol), SiO_2-SO_3H catalyst (10 mol%) was prepared in a small glass vial and the closed vial was heated in an oil bath at 130 °C for 6 h. The resulting mixture was diluted with 20 mL of *t*-butyl methyl ether, centrifuged at 1700*g* for 5 min to remove the catalyst. The supernatant was cooled to 0 °C in an ice bath and treated with excess diazomethane (4 equivalents, generated using Diazald and KOH) and allowed to warm to room temperature in 1 h, then left at room temperature for 24 h. The ether solution was then analyzed using GC–MS. A ^1H NMR analysis of the reaction product after removal of ether showed the quantitative conversion of carboxylic acids in the reaction mixture to the corresponding methyl esters. The GC–MS chromatogram is shown as Figure SD1 in the *supplementary data*. The mass spectra of five methyl ester products formed are included in the *supplementary data.*

2.4. Recyclability of the solid acid catalyst SiO_2-SO_3H in the dimerization of levulinic acid

A mixture of levulinic acid (116 mg, 1.0 mmol), and SiO_2-SO_3H (10 mol%) was prepared in a small round bottom flask and the closed flask was heated in an oil bath at 130 °C for 6 h. The resulting mixture was treated with 10 mL of *t*-butyl methyl ether, centrifuged at 1700*g* for 5 min to remove the catalyst. The catalyst was further washed with a second 10 mL portion of *t*-butyl methyl ether. The combined ether layer was evaporated to give the products. The recovered SiO_2-SO_3H catalyst was dried at 70 °C for 24 h, and was reused in the dimerization of levulinic acid using the same procedure. The percent yields of reusing the same catalyst sample in four catalytic cycles are shown in Fig. 3.

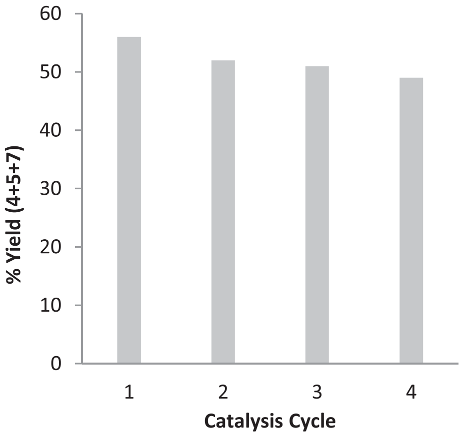


Fig. 3. Recyclability of the solid acid catalyst SiO_2-SO_3H in the in aldol dimerization of levulinic acid to a mixture of C10 lactone-acids. A mixture of levulinic acid (1.0 mmol), SiO_2-SO_3H (10 mol%), were used in all experiments, 130 °C, 6 h.

3. Results and discussion

3.1. Solid acid catalyzed dimerization of levulinic acid

Eight solid acid catalysts: Amberlyst-15, SiO_2-SO_3H, Dowex50WX8, Carbon-SO_3H, TiO_2-SO_3H, Al_2O_3-SO_3H, $H_3PW_{12}O_{40}$, and $Nb_2O_5.H_2O$ were screened for acid catalyzed condensation reaction of levulinic acids. Amberlyst-15, Dowex50WX8, SiO_2-SO_3H and $H_3PW_{12}O_{40}$ showed good to fair catalytic activity as shown in Table 1. The acid catalysts used are commercial materials or prepared using standard

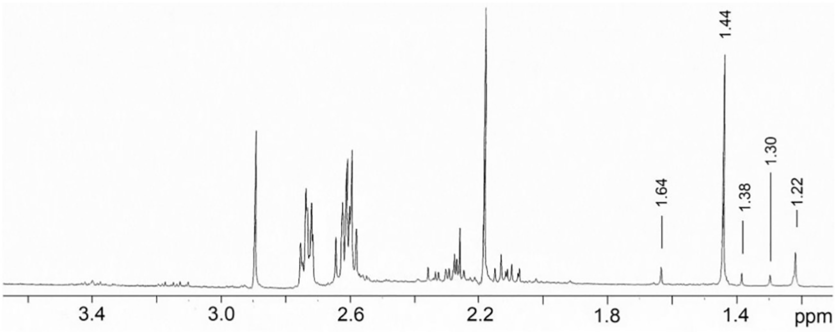


Fig. 2. ^1H NMR ($CDCl_3$) of the reaction mixture in SiO_2-SO_3H catalyzed aldol dimerization of levulinic acid. Levulinic acid (1.0 mmol), SiO_2-SO_3H (10 mol%), 130 °C, 6 h.

literature procedures and all are completely homogeneous materials and we believe the acid sites are homogeneously distributed on the surface of these catalysts. The products formed were identified by comparison of the NMR of the reaction mixture with published NMR data [12], conversion to methyl esters followed by GC–MS analysis and by a computational study on calculation of the relative energies of the optimized structures of all possible products.

A representative ^{1}H NMR spectrum of a reaction product mixture from entry 4 in Table 1 is shown in Fig. 2. The high field methyl signals below 1.8 ppm are due to the methyl groups of the levulinic acid dimerized products. The peak at 1.44 ppm is from the methyl group attached to the C2 of the lactone ring of the major product tetrahydro-2-methyl-5,γ-dioxo-2-furanpentanoic acid (**4**) in Fig. 1. The four smaller signals at 1.22, 1.30, 1.38 and 1.64 ppm are from the minor products; methyl groups of diastereomeric pairs of products: 3-(2-methyl-5-oxo-tetrahydrofuran-2-yl)-4-oxopentanoic acid (**6**) and 3-acetyl-2-methyl-tetrahydro-5-oxo-2-furanpropanoic acid (**7**) shown in Fig. 1. The product composition indicating the major product to all minor products ratio [**4**: (**6** + **7**)] could be determined by integration of these methyl signals in the ^{1}H NMR spectra and these data are in the last column of Table 1.

The ^{1}H NMR analysis of the product mixture was further supported by conversion of the lactone- acid product mixture to their methyl esters by treatment with diazomethane and GC–MS analysis. The total ion GC–MS chromatogram (9.3–12.3 min.) of the methyl ester product mixture is shown as Figure SD1 in the *supplementary data*. The major peak at 11.00 min. Can be assigned to the major product tetrahydro-2-methyl-5,γ-dioxo-2-furanpentanoic acid (**4**) in Fig. 1. The four smaller peaks at 10.27, 10.37, 10.74 and 10.84 min. Are from the diastereomeric pairs of products: 3-(2-methyl-5-oxo-tetrahydrofuran-2-yl)-4-oxopentanoic acid (**6**) and 3-acetyl-2-methyl-tetrahydro-5-oxo-2-furanpropanoic acid (**7**). The mass spectra (*supplementary material*) of the five methyl ester products further confirmed the formation of one major product and four minor products as a result of two diastereomeric pairs. All five mass spectra showed M + 1 molecular ion peaks at 229 corresponds to the levulinic acid dimer - lactone acid methyl ester molecular formula $C_{11}H_{16}O_5$. It is interesting to note that mass spectra of methyl esters eluted at 10.27 and 10.37 min. in the GC–MS shows similar mass spectra with prominent peaks at m/e 229, 169, 136 and 108; likely due to a pair of diastereomeric minor products. On the other hand methyl esters eluted at 10.74 and 10.82 min. Showed somewhat similar fragmentation patterns and both spectra showed a prominent peak at 211 due to the loss of a water molecule, which was not observed in the mass spectra of GC peaks at 10.27 and 10.37 min.; as these peaks are likely due to the other pair of diastereomeric products. The major compound eluted at 11.00 min. Showed prominent peaks at m/e 229, 211, and 115; which is different from the four minor products.

The proposed mechanism showing the possible acid catalyzed aldol condensation pathways are shown in Fig. 1. The C5 enol form of levulinic acid on condensation with a protonated second molecule of LA can form the intermediate diacid **2** (Fig. 1). This diacid can undergo lactonization in two possible pathways. The cyclization shown in blue arrows leads to the γ-butyrolactone system containing product **4**. On the other hand cyclization in the red arrows path gives substituted 2-oxepane-1,5-dione product **5**. The acid catalyzed aldol condensation via C3 enol form can lead to the intermediate diacid **3** (Fig. 1). This diacid may also undergo lactonization in two possible pathways. The blue arrows lead to the di-substituted γ-butyrolactone system containing product **6**. Alternatively cyclization in the red arrows path gives the tri-substituted γ-butyrolactone product **7**.

As another approach to assign the aldol dimerization products, we have calculated the relative energies of DFT B3LYP/6-31G* level optimized structures of all possible dimerization products **4–7**. The B3LYP/6-31G* level calculated relative energies are shown in Table 2 and the optimized structures are available in the *supplementary data* of this article. The C-5 enol path aldol product tetrahydro-2-methyl-5,γ-dioxo-2-furanpentanoic acid **4** is the thermodynamically most stable product and the major product in the reaction. The other three possible products **5**, **6** and **7** are thermodynamically less stable by +14.7, +4.4 and + 6.6 kcalmol^{-1} respectively (relative to **4**) as shown in Table 2. The least stable product by +14.7 kcalmol^{-1} would be 2-methyl-4,7-dioxo-2-oxepanepropanoic acid **5** with the 2-oxepane-1,5-dione ring system and therefore it is highly unlikely that this compound is formed in the dimerization reaction. Hence the computational study further confirms product **4** as the major product and diastereomeric pairs of products **6** and **7** as four minor products observed in NMR and GC–MS analysis of the methyl esters.

Table 2
Relative energies of DFT B3LYP/6-31G* optimized structures of all possible dimerization a products produced in solid acid catalyzed in aldol dimerization of levulinic acid. The optimized structures are available in the supplementary material.

Structure	E_{rel}/kcalmol^{-1}
4	0
5	+14.7
6	+4.4
7	+6.0

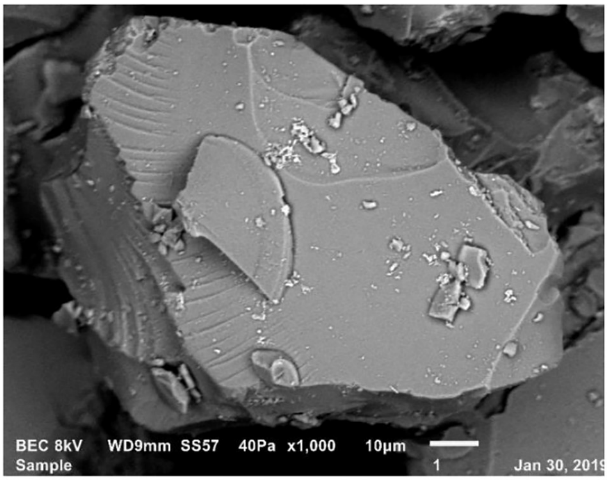
In the initial experiments using Amberlyst-15 and 5 mol% catalyst loading at 110 °C gave only 38% combined yield of all dimerized products, an increase in catalyst loading to 10 mol% and temperature to 130 °C produced higher yield of 43%. The SiO_2-SO_3H catalyst gave the highest yield of dimerized products and the initial experiments using 5 mol% SiO_2-SO_3H loading at 110 °C gave a 35% yield; increase in loading to 10 mol% and temperature to 130 °C produced the highest yield of 56%. However the increase in reaction time to 12 h at 130 °C caused a slight reduction in yield to 54% probably due to decomposition of products. We have tried to improve the levulinic acid conversions and product yields by changing reaction conditions with silica - sulfuric acid catalyst. The increase in catalyst loading from 10 to 20% caused no significant change in levulinic acid conversion, but caused a decrease in the product yield (entry 6), probably due to charring and polymerizations. The experiments at a lower temperature of 120 °C for 6 and 12 h gave lower LA conversions and product yields in comparison to 130 °C experiments, as shown in entries 7 and 8. The experiment at a much higher temperature of 140 °C (entry 9) caused a significant reduction in the yield with a relatively high LA conversion; this low product yield is most likely due to charring and polymerizations as well.

Two other catalysts Dowex50WX8 and $H_3PW_{12}O_{40}$ also gave reasonable yields of 37 and 32% respectively. Furthermore, the attempts to achieve the complete conversion of levulinic acid dimerization using longer reaction times and higher catalyst loadings were not successful. The other solid acid catalysts carbon-SO_3H, TiO_2-SO_3H, Al_2O_3-SO_3H and $Nb_2O_5.H_2O$ gave only poor yields of dimerization products. The differences in acid group density can be one of the major reasons for the origin of different reactivities in the solid acid catalysts since SiO_2-SO_3H with the highest acid group density of 5.2 mmol/g showed the highest activity. Then some catalysts with low acid densities like $H_3PW_{12}O_{40}$ (1.0 mmol/g) also showed good activity. Therefore other factors like geometry, nature of acid groups, as well as the other functional groups on the surface may also contribute to the differences in catalytic activities of these solid acid catalysts.

3.2. Reuse of SiO_2-SO_3H solid acid catalyst in aldol dimerization of levulinic acid

The percent yields of products produced in reusing SiO_2-SO_3H catalyst in the aldol dimerization of levulinic acid to a mixture of C10 lactone-acids is shown in Fig. 3. This experiment shows that catalyst can be reused for four cycles with some deactivation in catalytic activity

(a) Fresh SiO_2-SO_3H catalyst



(b) Used SiO_2-SO_3H catalyst

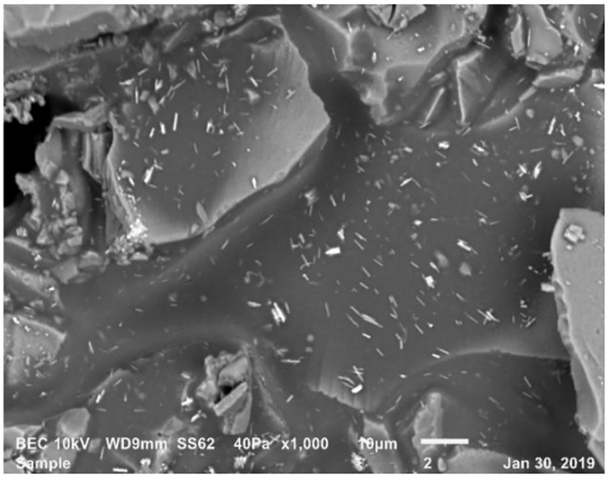


Fig. 4. SEM images of fresh (a) and used (b) SiO_2-SO_3H catalyst surfaces. Magnification ×1000.

of the SiO_2-SO_3H catalyst. In order to check the reason for catalyst deactivation and inability to improve the levulinic acid conversion we have analyzed the fresh and used catalyst surface with Scanning Electron Microscopy (SEM). The SEM image of the fresh catalyst shows a sharp image of a clean surface, whereas the used catalyst shows a dull surface without sharp edges (Fig. 4a and b). In addition, the white fresh catalyst turned into a dark brown powder after a single use as well. These changes in the SEM image and appearance may be due to the deposition of carbon or a polymer layer on the catalyst surface during the reaction. This contamination of the catalyst surface can cause the deactivation of the catalyst. The levulinic acid conversion (%) is shown in column 6 of the Table 1; practically in all experiments, the levulinic acid conversions are greater than the total product yields. This difference may be due to the loss of some starting materials to form carbon and polymeric byproducts. This difference in mass balance is further supported by color change and SEM images of the SiO_2-SO_3H catalyst showing some surface contamination.

4. Conclusion

We have shown that solid acid catalysts can be used to upgrade levulinic acid by aldol condensation type dimerization to a mixture of C10 lactone-acids. The major dimerization product was identified as tetrahydro-2-methyl-5,γ-dioxo-2-furanpentanoic acid formed via the aldol condensation of C5 enol form of levulinic acid. In addition four minor products were identified as diastereomeric pairs of 3-(2-methyl-5-oxo-tetrahydrofuran-2-yl)-4-oxopentanoic acid and 3-acetyl-2-methyl-tetrahydro-5-oxo-2-furanpropanoic acid arising from the aldol condensations of C3 enol form of levulinic acid by using a combination of spectroscopic and computational methods. The highest total yield 56% was obtained with the use sulfonated silica as the solid acid catalyst and the reminder of the mass balance was unreacted levulinic acid. The sulfonated silica catalyst could be recycled four times with a small loss in catalytic activity.

Acknowledgements

We thank United States National Science Foundation (NSF) grants CBET-1336469, CBET-1704144, HRD-1036593, and United States Department of Agriculture (USDA) grant CBG-2010-38821-21569 for financial support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2019.02.022.

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