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Citation for final published version:

Chaffey, Dawn R., Bere, Takudzwa, Davies, Thomas E., Apperley, David C., Taylor, Stuart H. and Graham, Andrew E. 2021. Conversion of levulinic acid to levulinate ester biofuels by heterogeneous catalysts in the presence of acetals and ketals. *Applied Catalysis B: Environmental* 293 , 120219. 10.1016/j.apcatb.2021.120219

Publishers page: <http://dx.doi.org/10.1016/j.apcatb.2021.120219>

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# Conversion of Levulinic Acid to Levulinate Ester Biofuels by Heterogeneous Catalysts in the Presence of Acetals and Ketals

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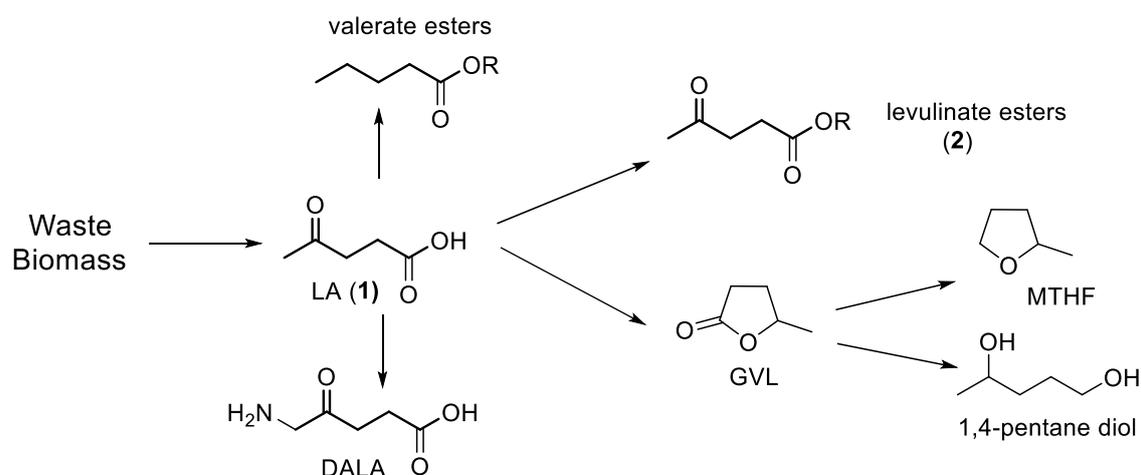
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**ABSTRACT:** The esterification of levulinic acid under acidic conditions to produce levulinate esters is of current significant interest due to the potential of these compounds as fuels and fuel additives. While a number of bespoke heterogeneous catalysts have been reported to be effective for this transformation, the use of widely available commercial catalysts has generally proved to be ineffective, with only low conversions to ester products being achieved. Herein, we report a novel strategy for the efficient synthesis of levulinate esters from levulinic acid in the presence of trialkyl orthoformates or dialkyl acetals and ketals catalyzed by commercial catalysts, such as ZSM-5 and Amberlyst-15. These reactions proceed under mild conditions and in short reaction times to selectively produce high yields of levulinate esters.

**KEYWORDS:** esterification: heterogeneous catalysis: levulinate esters: bio-renewable fuel additives:

## 1. Introduction

An increased awareness of global climate change, allied to an increasing demand for fossil fuel resources, has led to the development of strategies for the production of energy, fuels and feedstock chemicals employing more sustainable approaches [1,2]. These factors have been critical to the current interest in biomass valorisation, and in particular, the valorisation of inedible lignocellulosic residues which are sustainably sourced from agriculture and forestry activities, and which offers a low cost and abundant source of materials for the production of platform chemicals [3,4]. Levulinic acid **1** (LA), derived from the acid catalyzed hydrolysis of cellulose, is one of the most important of these new bio-derived platform molecules which, due to its high functionality, can be converted into a variety of valuable consumer products. Numerous reports have detailed elegant synthetic approaches for the transformation of bio-derived levulinic acid into lactones, saturated and unsaturated heterocycles and long chain fatty acids, alkenes and alkanes. (**Scheme 1**) [5–9].

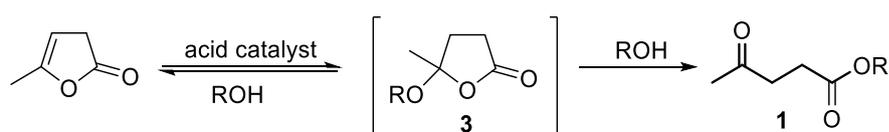


### Scheme 1: Applications of levulinic acid as a bio-derived platform chemical

The most common approach to LA upgrading, however, is direct Fischer esterification in the presence of alcohols under acidic conditions to produce levulinate esters **2**, which are of use in the food flavouring industry, as solvents and as plasticisers.

However, it is as a fuel additive and biofuel source which is the most important application of levulinate esters given their low toxicity, high flashpoints and flow properties [12,13]. Fischer esterification of LA is typically achieved under acidic conditions using homogeneous mineral acid catalysts, such as sulphuric acid, hydrochloric acid or phosphoric acid, producing high yields of product in short reaction times. These catalysts, however, are not easily recyclable and present additional challenges in both product isolation, by-product formation, waste stream management and equipment maintenance. Thus, the implementation of heterogeneous alternatives which avoids these limitations, is a highly desirable objective. The use of widely available commercial catalysts, such as zeolites, or macroreticular acidic resins, has generally provided disappointing results, with only low conversions to ester products being observed. Indeed, conversions employing zeolite catalysts typically do not exceed 10%, with Amberlyst-15 providing ~50% conversion [14–16]. This has led to the development of a range of alternative catalyst for this transformation, which although more effective than zeolites or resins, require prior synthesis making them unattractive for industrial scale applications [17–21]. The reasons behind the disappointing performance observed with zeolites and resins is complicated, and has been the subject of numerous reports with various factors being identified as impacting strongly on catalyst performance. These include swelling characteristics of the resins, access to acidic sites within the pore structure, overall acidity, the strength and type of acid sites present, pore structure and the hydrophobicity of the active sites, and the mechanism of the esterification process itself [14,17].

Our interest in this area was prompted by recent work concerning LA esterification reactions from  $\alpha$ -angelica lactone that identified the formation of pseudo lactone **3** as an intermediate which once formed, can react further to produce levulinate esters (**Scheme 2**) [22,23].



**Scheme 2: Levulinate ester formation from  $\alpha$ -angelica lactone**

This alternative approach to levulinate esters is highly attractive as it avoids the most common pitfalls associated with the Fischer esterification process, and exploits the natural tendency of lactols to undergo ring opening reactions with nucleophiles [24–26].  $\alpha$ -Angelica lactone, however, requires prior synthesis from levulinic acid under very high temperature and low-pressure reaction conditions, and such a circuitous route would not be economically viable [27]. We reasoned, however, that if the lactonization reaction could be optimized directly from levulinic acid itself, then a more efficient protocol could be developed in which the pseudo lactone acts as an advanced intermediate for further elucidation not only into levulinate esters, but also potentially to a range of related products. We identified a strategy in which the ketone moiety of LA is activated toward intramolecular cyclization by reaction with an acetalization reagent, such as trimethylorthoformate (TMOF) or dimethoxypropane (DMOP), to produce the lactol **3**. This approach provides an interesting and potentially more flexible strategy for the synthesis of levulinate ester and related derivatives. Herein we disclose our initial studies in this area, and report the development of a highly efficient esterification protocol for the conversion of levulinic acid into levulinate esters catalyzed by commercially available catalysts, such as ZSM-5 and Amberlyst-15 in the presence of trialkyl orthoformates and dialkyl acetals.

## 2. Experimental

### 2.1 Chemicals and catalysts

Commercially available materials were used as received. Alcohol solvents were stored over activated 3Å molecular sieves prior to use. ZSM-5-(30) was purchased in its  $\text{NH}_4^+$  form and calcined at 500 °C for 3 hours to provide the  $\text{H}^+$  form. The nanoporous alumino- and borosilicate catalysts employed here were synthesized using evaporation-induced self-assembly (EISA) methodology as described previously, and characterized employing literature procedures [28–32]. All catalysts were stored at 140 °C for at least 12 hours prior to use. Amberlyst-15 was dried overnight under vacuum prior to use and stored in a desiccator.

## 2.2 Catalyst testing and product characterization

All reactions were carried out in a stirred batch reactor. Product mixtures were analyzed by  $^1\text{H}$  NMR recorded at 400 MHz in  $\text{CDCl}_3$  at 25 °C and by GC–MS techniques. Percentage yields and selectivity were determined from quantitative  $^1\text{H}$  NMR experiments using *para*-xylene as the internal standard by integration of the relevant signals from crude spectra [33,34]. GC-MS analysis was performed using a Thermo Scientific Trace 1300 GC and Thermo Scientific TSQ 8000 Evo MS employing a VF-5ms capillary column (30m, 0.25mm i.d. and 0.25 $\mu\text{m}$ ) and a gradient temperature profile with an initial temperature of 50 °C for 3 minutes rising to 280 °C at a rate of 20 °C  $\text{min}^{-1}$ .

## 2.3 Typical experimental procedure for the synthesis of methyl levulinate employing trimethyl orthoformate

ZSM-5-(30) (40 mg) was added to a solution of levulinic acid (116 mg, 1 mmol) and trimethyl orthoformate (104 mg, 1 mmol) in dimethyl carbonate (2 mL) in a sealed reaction vessel and heated to 75 °C for 3 hours. On completion of the reaction, the crude reaction mixture was analysed by quantitative  $^1\text{H}$  NMR analysis.

## 2.4 DRIFTS pyridine adsorption measurements

DRIFTS measurements were recorded from 1000–4000  $\text{cm}^{-1}$  at a spectral resolution of 4  $\text{cm}^{-1}$  (64 scans) on a Bruker Tensor 27 spectrometer fitted with a mercury cadmium telluride (MCT) detector cooled by liquid  $\text{N}_2$ . A sample was loaded into the Praying Mantis high-temperature (HVC-DRP-4) *in situ* cell before exposure prior to evacuation under vacuum (pressure lower than 10 $^{-6}$  mbar) at 400 °C for 1 hour. A background spectrum was recorded at 150 °C under  $\text{N}_2$  flow (30  $\text{mL min}^{-1}$ ). The sample was then exposed to pyridine (8 mL) by the isothermal saturator (14.0 °C) under  $\text{N}_2$  flow (30  $\text{mL min}^{-1}$ ) at 150 °C for 30 minutes. Excess adsorbate was removed by outgassing at the same temperature for 1 hour prior to recording spectra.

### 3. Results and discussion

#### 3.1 Catalyst characterization

All of the porous silicate materials displayed the expected large surface areas and narrow pore size distributions expected (**Table 1**). The physical properties of commercially available ZSM-5-(30) were consistent with previous literature reports [35], and both it and Amberlyst-15 [36] displayed significantly greater acidity than the nanoporous aluminosilicate materials produced using the EISA approach.

**Table 1**  
**Chemical and Physical Properties of the Catalysts**

Catalyst	Si/Al Gel Composition	Si/Al (EDX) <sup>a</sup>	BET Surface Area (m <sup>2</sup> g <sup>-1</sup> ) <sup>b</sup>	Total Acidity (μmol g <sup>-1</sup> ) <sup>c</sup>	Pore Width (nm) <sup>d</sup>
ZSM-5-(30)	30	19	405	1450	0.82
Amberlyst-15	-	-	45 <sup>e</sup>	4700 <sup>e</sup>	25 <sup>e</sup>
Al-13-(2.34)	13	14	614	440	2.34
B-13-(3.54)	13	-	1095	590	3.54

<sup>a</sup> Determined by energy dispersive X-ray (EDX) analysis.

<sup>b</sup> Obtained by the Brunauer–Emmett–Teller (BET) method.

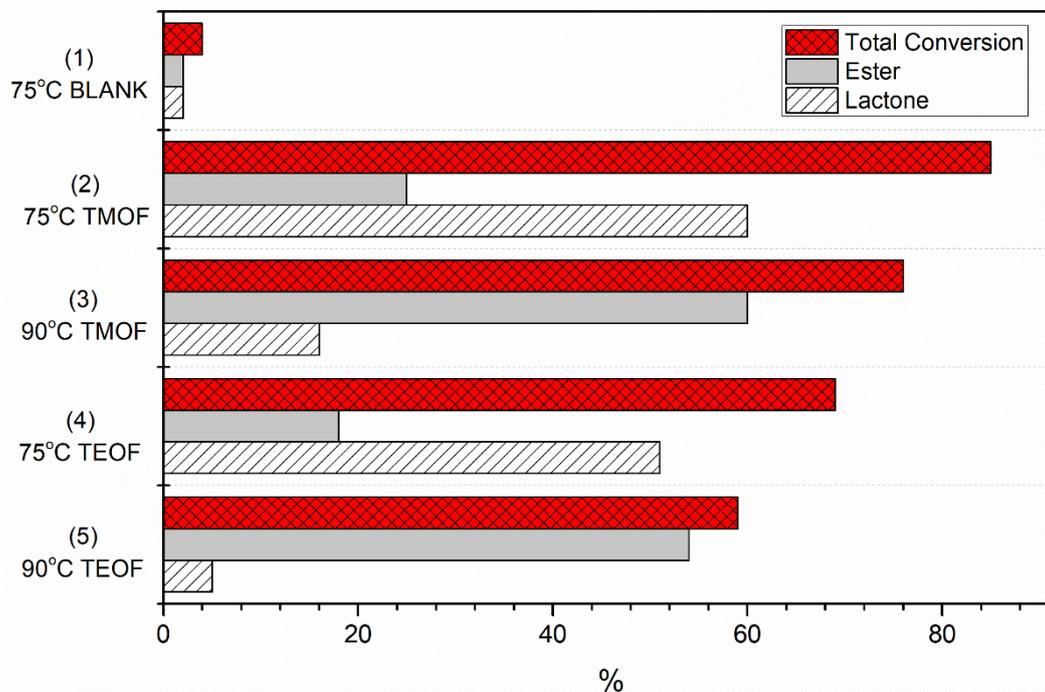
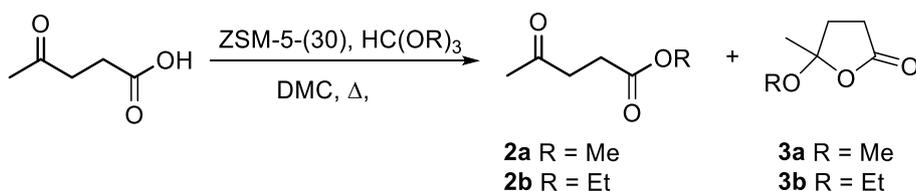
<sup>c</sup> Determined by temperature programmed desorption (TPD) analysis.

<sup>d</sup> Determined by the non-linear density function theory (NLDFT) method.

<sup>e</sup> Literature values.

#### 3.2 Reactions of LA catalyzed by ZSM-5-(30) in the presence of trialkyl orthoformates

We initially investigated the reaction of LA with methanol catalyzed by ZSM-5-(30) at 75 °C. Control reactions were carried out to verify the poor performance of this catalyst in methanol which were consistent with previous literature reports [16]. Furthermore, carrying out the esterification reaction of **1** in dimethyl carbonate (DMC) in the presence of ZSM-5-(30) provided no ester products, indicating that no significant degradation of DMC with subsequent release of methanol, was occurring under the reaction conditions [37]. Furthermore, reactions in the absence of ZSM-5-(30) provided no ester or pseudo lactone products, suggesting that the level of autocatalysis by LA is minimal.



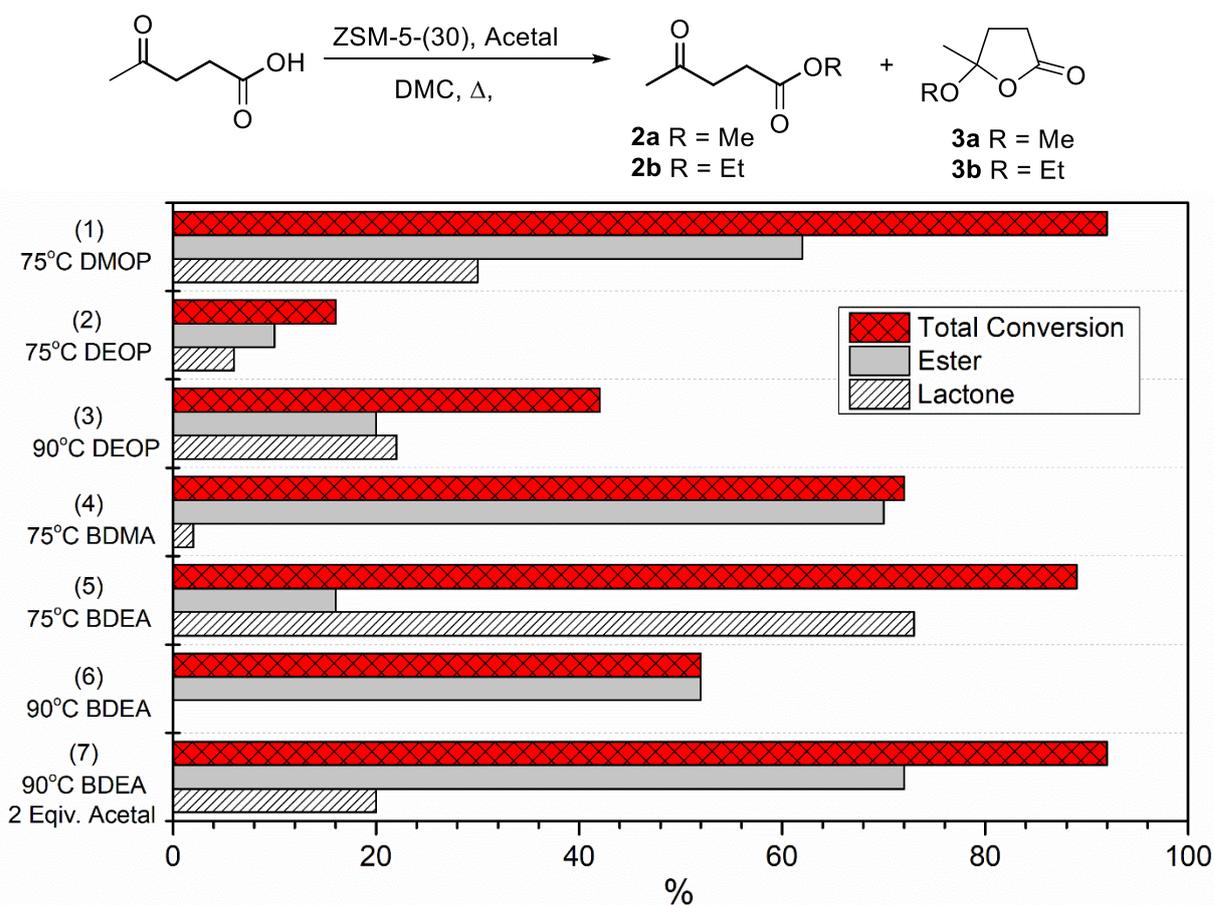
**Figure 1.** ZSM-5-(30) catalyzed esterification reactions of levulinic acid in DMC in the presence of trialkyl orthoformates (40 mg of catalyst, 1 equivalent of orthoformate, 3h reaction at the specified temperature).

Gratifyingly, reactions in the presence of one equivalent of TMOF gave good yields of pseudo lactone **3a** with moderate selectivity over the levulinate ester **2a** being observed (**Figure 1**). The selectivity of the reaction for **2a** over **3a** could be reversed simply by increasing the reaction temperature from 75 °C to 90 °C, and under these conditions, high conversions to methyl ester **2a** were achieved. Similarly, introducing one equivalent of triethyl orthoformate (TEOF) provided good yields of the corresponding ethyl pseudo lactone **3b** or ethyl levulinate ester **2b** on variation of the reaction temperature as above. The performance of zeolite materials in LA esterification reactions has been attributed to their pore structure, and how well they can accommodate the intermediates and transition states involved in the esterification process [14]. In general, ZSM-5 has been demonstrated to perform poorly in Fischer esterification reactions, and the much-improved performance observed here may be taken as being indicative that a different esterification mechanism is in operation in these reactions. Interestingly, the

formation of products derived from the acetalization of LA were not observed in the  $^1\text{H}$  NMR spectra of the crude reaction mixtures. This does not discount the possibility that these intermediates are involved in the formation of pseudo lactones and indeed, previous literature reports have demonstrated the highly facile nature of this cyclization reaction under acidic conditions [38,39]. Furthermore, none of the corresponding products derived from subsequent acetalization of esters **2a** or **2b** were observed in the crude reaction mixtures.

### *3.3 Reactions of LA catalyzed by ZSM-5-(30) in the presence of acetals and ketals*

We next considered the corresponding esterification reaction employing commercially available acetals and ketals, in which acetalization of LA occurs by an acid catalyzed acetal exchange reaction. We initially investigated the ketal DMOP as the acetalization reagent under our standard reaction conditions, which provided high conversions of LA to give an approximate 2:1 mixture of **2a** and **3a** (**Figure 2**). Disappointingly, however, the use of diethoxy propane (DEOP) provided only moderate conversions of LA, even at elevated temperatures, giving approximately equal quantities of **2b** and **3b**. The poor yields observed here are presumably due to the facile hydrolysis of ketal reagents under the reaction conditions. Switching to acetal reagents, such as benzaldehyde dimethyl acetal (BDMA) proved to be highly successful, providing excellent conversions to **2a**. Benzaldehyde diethyl acetal (BDEA) provided high yields of lactone **3b** at lower reaction temperatures with high yields of **2b** being achieved at elevated temperatures in the presence of a small excess of acetal reagent. It is noteworthy that reactions carried out employing the corresponding alcohol as solvent in the presence of acetals provided inferior yields of levulinate esters, indicating that the high yields achieved are not simply due to the acetal acting as a dehydrating agent. As with the case of trialkyl orthoformates previously, no acetals derived from LA or ester products were observed in the  $^1\text{H}$  NMR spectra of the crude reaction mixtures.



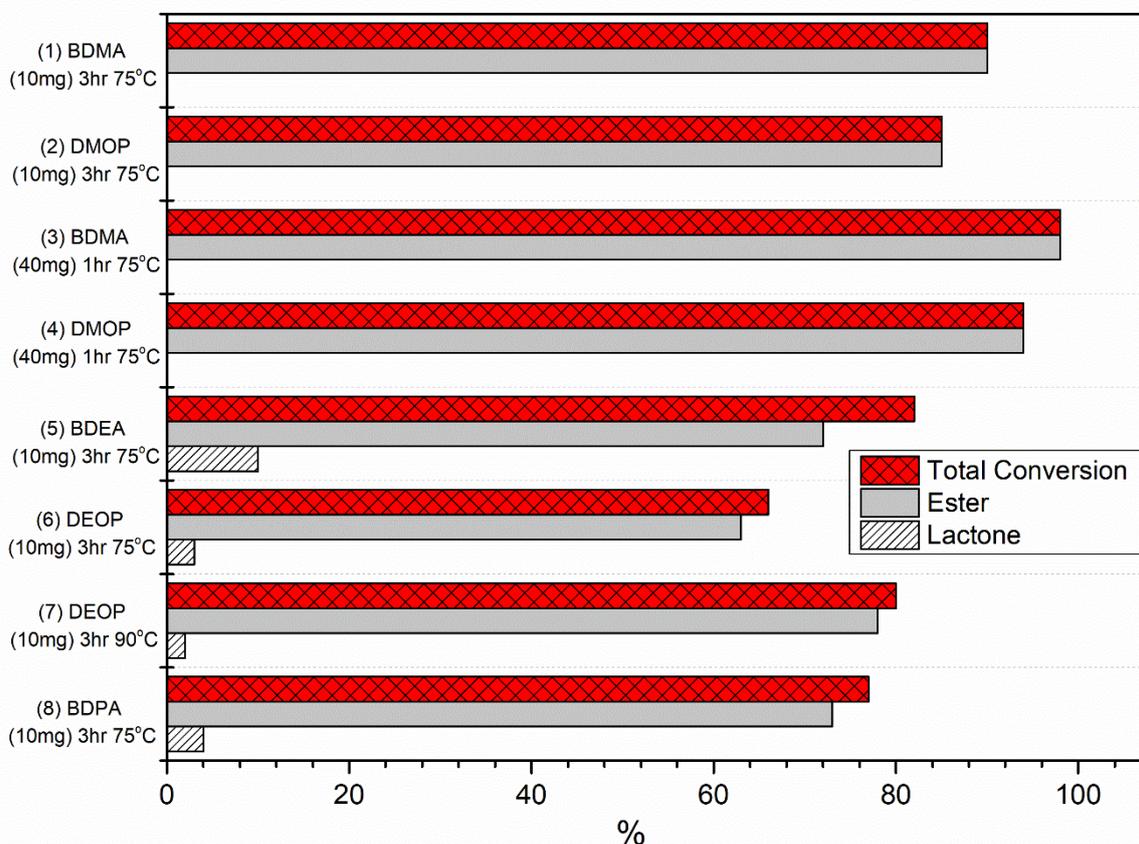
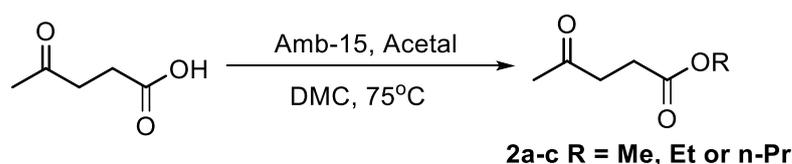
**Figure 2.** ZSM-5-(30) catalyzed esterification reactions of levulinic acid in DMC the presence of acetals and ketals (40 mg of catalyst, 1 equivalent of acetal/ketal, 3h reaction at the specified temperature).

### 3.4 Reactions of LA catalyzed by Amberlyst-15 in the presence of dimethyl and diethyl acetals and ketals

We next investigated the formation of levulinate esters catalyzed by strongly acidic ion exchange resins, which are among the most widely employed industrial catalysts. Given that these materials have been demonstrated to be highly effective in a range of acid catalyzed reactions including esterification and etherification [40,41], the lack of an effective synthetic protocol for the synthesis of levulinate esters using these materials is surprising. As discussed previously, studies in this area have indicated that the activity of these resins can be tentatively correlated to their pore structure and physical properties [15]. Amberlyst-15 resin generally performs poorly, giving only moderate yields of ester products, even after extended reaction times at elevated temperatures. This is attributed to the high degree of cross-linking which results in poor swelling characteristics, and hence poor access to

active sites within the pore structure [15]. In such cases, only the easily accessible surface sites are available to catalyze the reaction. Amberlyst-15 has also been reported to be a highly effective catalyst for acetal formation, both directly from trialkyl formates and carbonyl compounds and by transacetalization [42,43], and we were intrigued as to whether a comparable increase in LA conversion would also be observed in this case.

Our initial studies investigated low catalyst loadings of Amberlyst-15 (10 mg) to verify previous literature reports of poor catalyst performance in alcohol solvents. As previously observed with zeolites, the reaction of LA in DMC in the presence of Amberlyst-15 provided only trace quantities of ester product, indicating only minimal degradation of DMC was occurring under the reaction conditions.



**Figure 3.** Amberlyst-15 catalyzed esterification reactions of levulinic acid in DMC in the presence of dimethyl acetals and ketals (1 equivalent of acetal/ketal, reactions carried out at the specified temperature for the specified time).

As previously, we were delighted to observe that the esterification reactions carried out in DMC in the presence of BDMA or DMOP proceeded efficiently giving high yields of **2a** at 75 °C (**Figure 3**). As expected, increased loadings of Amberlyst-15 gave improved yields of ester, with reactions in the presence of BDMA or DMOP providing near quantitative conversions of LA to **2a** in short reaction times. Excellent conversions were also achieved on switching to acetals and ketals derived from ethanol (BDEA and DEOP) and propanol (benzaldehyde dipropyl acetal, BDPA) which also proceeded readily to give high conversions to **2b** and **2c**. In the case of DEOP, yields were improved, and reaction times shortened, by employing elevated temperatures (90°C).

### 3.5 Recycling and reusability studies

To complete our studies in this area, we conducted a short study to assess catalyst recyclability and reusage. Numerous studies have demonstrated the recyclability of zeolite catalysts in a wide range of transformations [36,44,45], and indeed, we have demonstrated that ZSM-5-(30) can effectively be recycled from related etherification reactions employing acetals and orthoformates [37]. Similarly, Amberlyst-15 has also been demonstrated to be recyclable from Fischer esterification reactions and to retain its activity over the course of a number of cycles. In agreement with these previous literature studies [14], the Amberlyst-15 catalyst was found to be fully recyclable and displayed no reduction in its catalytic activity over the course of three re-uses (**Table 2**).

**Table 2. Re-usability of Amberlyst-15 in esterification reactions of levulinic acid<sup>a</sup>**

Entry	Ester (%) <sup>b</sup>	Conversion (%) <sup>b</sup>
Initial use	93	>95
1 <sup>st</sup> reuse	95	>95
2 <sup>nd</sup> reuse	94	>95
3 <sup>rd</sup> reuse	94	>95

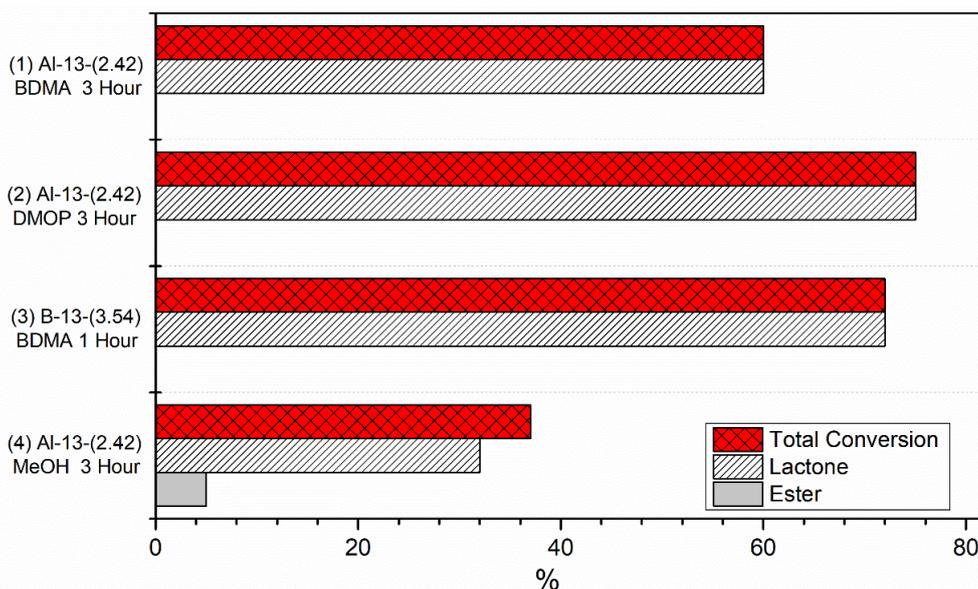
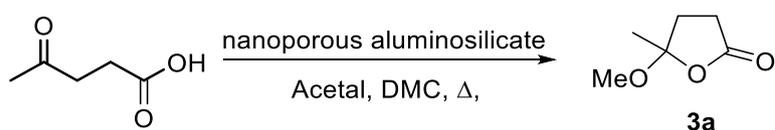
<sup>a</sup> Experimental conditions: Amberlyst-15 (40 mg) was added to a solution of LA and DMOP (1 mmol) in DMC (2 mL) at 75 °C for 1 hour.

<sup>b</sup> Determined by quantitative <sup>1</sup>H NMR of the crude reaction mixture.

### 3.6 Reactions of LA catalyzed by nanoporous silicate materials in the presence of acetals and ketals

We were intrigued as to whether the esterification reaction employing acetals and orthoformates was general, and also whether the selectivity of the reaction could be controlled by employing silicate materials displaying different physical properties rather than by varying the temperature. We have demonstrated that nanoporous aluminosilicate and borosilicate materials can be easily synthesised from silicate precursors employing an evaporation-induced self-assembly (EISA) approach. The physical properties of these silicates, such as pore size, the number of Lewis/Brønsted acid sites as well as overall acidity, can be easily modified through judicious choice of reaction conditions to provide a highly flexible route to a range of novel catalytic materials. We were particularly interested in comparing the activity of a nanoporous aluminosilicate material, Al-13-(2.42), which we have previously demonstrated to be highly effective in the formation of acetals either directly from alcohols and carbonyl compounds, or by acetal exchange processes [46,47]. In addition to having a larger pore size than ZSM-5-(30), which should ensure enhanced access to the catalytic sites, this material also displays significantly reduced overall acidity in comparison. The observation in these studies that the highly acidic Amberlyst-15 material generally provided little or no pseudo-lactone products at elevated temperatures while producing high yields of levulinate esters is indicative that the subsequent ring-opening step of the esterification reaction is controlled by the overall acidity of the material. Initial reaction employing Al-13-(2.42) in the presence of BDMA proceeded rapidly to provide high conversions to the pseudo lactone **3a** with excellent selectivity over the corresponding ester product. (**Figure 4**).

The Al-13-(2.42) material was also effective in the presence of DMOP, providing similar yields and selectivity to reactions carried out with BDMA. Switching to the borosilicate material B-13-(3.54), which displays predominantly Lewis acidity, also provided high conversions of LA to **3a** again with excellent selectivity.

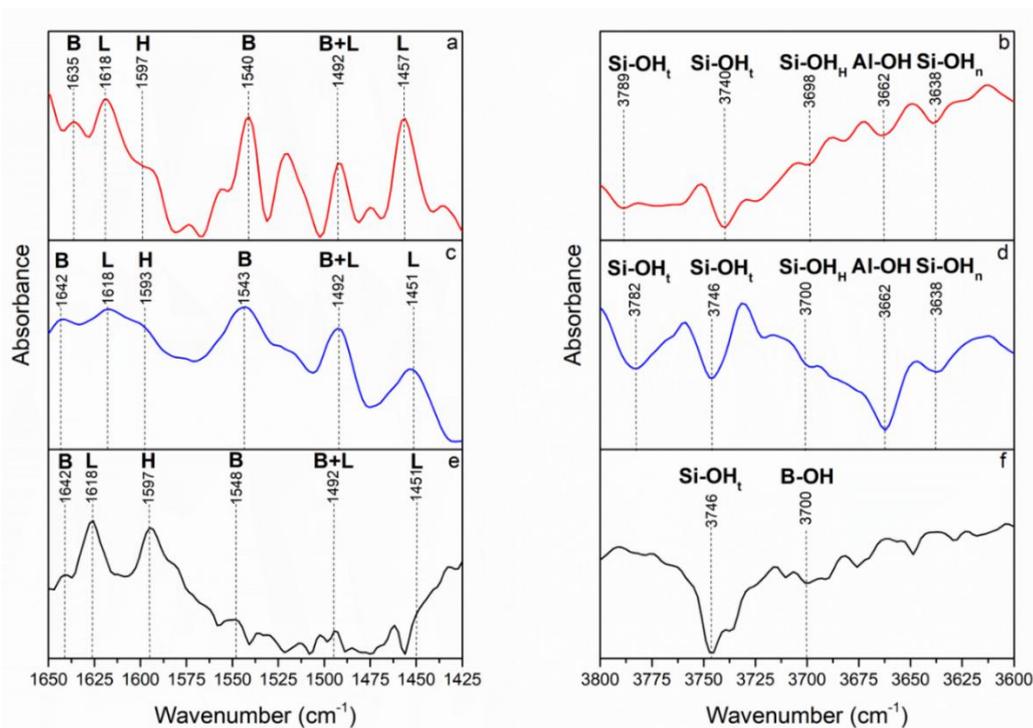


**Figure 4.** Nanoporous silicate catalyzed esterification reactions of levulinic acid in DMC in the presence of acetals and ketals (40 mg of catalyst, 1 equivalent of acetal/ketal at 75 °C).

Presumably, the difference in product profile observed with these nanoporous catalysts as compared to ZSM-5 and Amberlyst-15 is due to their much reduced acidity, which is sufficient to catalyze the formation of the hemiacetal product, and subsequent formation of the pseudo lactone product, but is not sufficient to catalyze the formation of the ester product. A similar dependence on acidity has previously been observed in the formation of pseudo lactones and levulinate esters from  $\alpha$ -angelica lactone [22]. Interestingly, reactions carried out with higher catalyst loadings (80mg) of Al-13-(2.42) using methanol as solvent proceeded efficiently to give moderate yields of the pseudo-lactone with similarly high selectivity.

### 3.7 DRIFTS pyridine adsorption studies

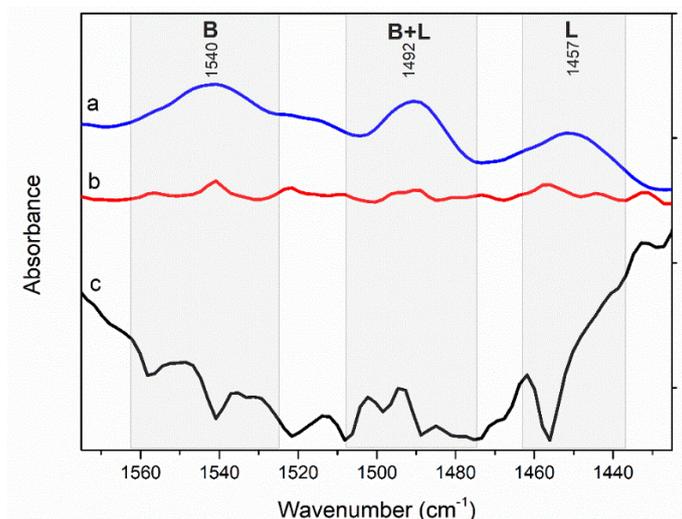
The acidic properties of ZSM-5-(30) and the mesoporous borosilicate B-13-(3.54) and aluminium silicate Al-13-(2.42) materials were investigated by diffuse reflectance FT-IR (DRIFTS) analyses. Spectra obtained after pyridine adsorption at 150 °C for the ranges spanning 1650–1400  $\text{cm}^{-1}$  and 3800–3600  $\text{cm}^{-1}$  are shown in **Figure 5a–e**.



**Figure 5.** FT-IR spectra of pyridine adsorbed at 150 °C and after evacuation at 400 °C for the Lewis and Brønsted acid site stretching region (1650–1400  $\text{cm}^{-1}$ ) and hydroxyl (OH) stretching region (3800–3500  $\text{cm}^{-1}$ ) on (a & b) Al-13-(2.42); (c & d) ZSM-5-(30); and (e & f) B-13-(3.54) catalysts.

Analysis of the OH stretching region of ZSM-5-(30) (**Fig 5d**) are in close agreement with previous literature reports, and show the expected major bands at 3662  $\text{cm}^{-1}$  and 3746  $\text{cm}^{-1}$  attributed to the extraframework AlOH groups and terminal silanol groups SiOH along with the minor stretches associated with internal H-bonded SiOH [48]. Similarly, inspection of the 1425–1650  $\text{cm}^{-1}$  region (**Fig 5c**) shows the typical bands associated with Lewis and Brønsted acid sites at 1451  $\text{cm}^{-1}$  and 1543  $\text{cm}^{-1}$  respectively, with the band at 1492  $\text{cm}^{-1}$  being due to the interaction of pyridine with both types of site. The overall acidity reported for comparable ZSM-5-(30) samples is significantly lower than that determined in our TPD analysis (Table 1) and presumably reflects the reduced accessibility of the bulky pyridine molecules to the acid sites [49,50]. Access of substrates to acid sites has been identified as a critical factor in rationalising the activity displayed by zeolite catalysts in esterification reactions, and in particular, to the Brønsted acid sites which are responsible for catalytic activity in Fischer esterification reactions [51].

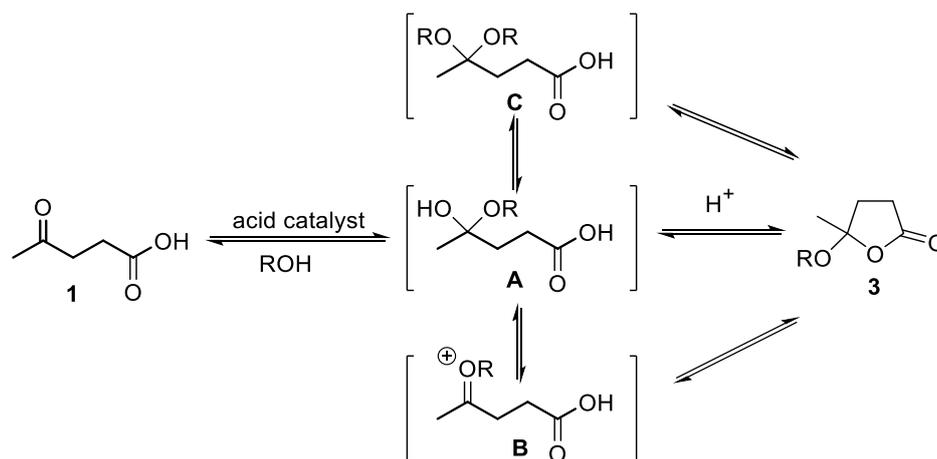
Direct comparison of the species present is shown in **Figure 6** and it is apparent that both the Brønsted and Lewis acid strength and site density is markedly lower in both the Al-13-(2.42) and B-13-(3.54) samples compared to the ZSM-5-(30) catalysts and is in keeping with NH<sub>3</sub> TPD measurements (**Table 1**).



**Figure 6.** FT-IR spectra of pyridine adsorbed at 150 °C and after evacuation at 400 °C presented at the same scale for direct comparison of the Lewis and Brønsted acid site stretching region (1650–1400 cm<sup>-1</sup>) on (a) ZSM-5-(30); (b) Al-13-(2.42); and (c) B-13-(3.54) catalysts.

### 3.8 Mechanistic Considerations

The formation of the pseudo lactone **3** from levulinic acid has been proposed to occur through the formation of a hemiacetal intermediate (**Scheme 3**, intermediate **A**), which once formed undergoes intramolecular cyclization [52,53]. It should be noted, however, that the cyclization can also be envisaged to proceed through either a discrete oxonium ion (**B**) or indeed directly from the acetal (**C**) itself [38,39]. All of these species have previously been identified as intermediates in the formation of acetals from carbonyl compounds, a well understood and well-studied reaction which is routinely achieved under acid catalysis in the presence of trialkyl orthoformate reagents or acetals [54,55]. Acetals have also been demonstrated to function as highly effective surrogates for the carbonyl group, displaying enhanced reactivity toward nucleophiles in a range of transformations including lactol formation [38,39,47,56].



### Scheme 3: Pseudo lactone formation from levulinic acid

The improved performance of both ZSM-5-(30) and Amberlyst-15 observed in these studies might best be explained by considering a change in mechanism from the classical Fischer mechanism to one involving the lactol intermediate. We propose that one of the reactive intermediates A–C is produced by reaction of the ketone carbonyl group of levulinic acid with the acetal or orthoformate reagent under the reaction conditions which then undergoes intramolecular cyclization to produce lactol **3**. The levulinate ester product is then produced by a subsequent ring-opening reaction catalysed by the acidic ZSM-5-(30) or Amberlyst-15 catalysts but not by the less acidic alumino- or borosilicate materials. It would be expected that the lactol intermediate would be easily produced under these reaction conditions, given the previously documented success in acetalization protocols employing these catalysts [42,57]. The observed differences in product distribution are therefore dependent on the acidity of the catalyst, with the highly acidic Amberlyst-15 catalyst efficiently catalysing the subsequent ring-opening of the lactone to give only ester product, and the less acidic ZSM-5-(30) requiring elevated temperatures. In agreement with previous literature observations concerning the ring-opening of lactone **3** [22], the nanoporous Al-13-(2.34) and B-13-(3.54) materials, which display significantly less acidity, are able to efficiently catalyse lactone formation but are not sufficiently acidic to catalyse the subsequent ring-opening reaction and ester formation.

## Conclusions

In conclusion, we have demonstrated that commercially available catalysts, such as ZSM-5-(30) and Amberlyst-15, efficiently catalyze the esterification reactions of levulinic acid in the presence of trialkyl orthoformates or acetals, providing the corresponding levulinate esters in high yields. This is in contrast to previous literature reports in which these catalysts perform poorly in the Fischer esterification reaction. In this new protocol, LA is initially activated by reaction of the ketone moiety with the acetalization reagent to produce a reactive intermediate which undergoes facile intramolecular cyclization to produce the pseudo lactone intermediate **3**. This then undergoes a subsequent ring-opening reaction with an alcohol species under acid catalysis. In the case of ZSM-5-(30), reactions carried out at low temperatures provide the pseudo lactone product **3** as the major product of the reaction, whilst higher reaction temperature provides access to ester products with high selectivity. Low loadings of the highly acidic ion exchange resin Amberlyst-15 efficiently catalyze the esterification reaction selectively producing the levulinate ester product even at low reaction temperatures, with higher catalyst loadings providing near quantitative yields of ester products. Nanoporous alumino- and borosilicate catalysts, which display significantly reduced acidity in comparison, effectively catalyze the formation of pseudo lactone products **3a** and **3b** under mild reaction conditions but are not sufficiently acidic to catalyze the subsequent ring-opening reaction. In all cases, the orthoformate or acetal reagents provide a source of the requisite alcohols and allows non-polar solvents to be employed, so avoiding the necessity to use polar alcohol solvents. Both ZSM-5-(30) and Amberlyst-15 are fully recyclable and easily recoverable providing additional improvements in overall efficiency.

## Notes

The authors declare no competing financial interest.

## **ASSOCIATED CONTENT**

### **Supplementary Information**

Catalyst characterization data.

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