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# Preparation of Biomass-Derived Furfuryl Acetals by Transacetalization Reactions Catalyzed by Nanoporous Aluminosilicates

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ABSTRACT: Nanoporous aluminosilicate materials efficiently catalyze the formation of furfuraldehyde dimethyl acetal directly from methanol in high yields and in short reaction times. The facile nature of this reaction has led to the development of a telescoped protocol in which the acyclic acetal is produced *in situ* and subsequently functions as a substrate for a transacetalization reaction with glycerol to produce the corresponding dioxane and dioxolane products which are potentially useful biofuel additives. These products are generated in high yield without the requirement for high reaction temperatures or prolonged reaction times, and the aluminosilicate catalysts are operationally simple to produce, are effective with either purified furfuraldehyde or crude furfuraldehyde and are fully recyclable.

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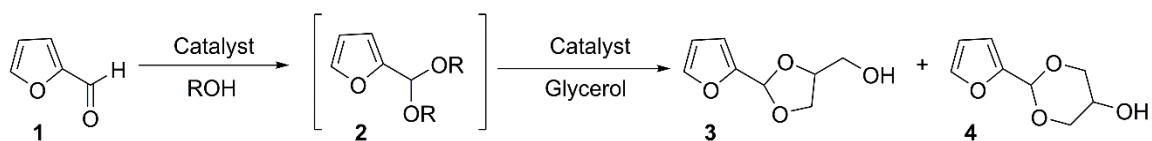
## INTRODUCTION

Current interest in the development of alternative strategies for energy production which have reduced environmental impact is of significant importance given the increase in demand for resources derived from fossil fuels. In particular, the demands of the transportation market have highlighted the need to develop fuels sources that are derived from more sustainable and renewable carbon sources. Of these, biomass valorization has attracted considerable interest as a sustainable and renewable solution to both energy and fuel requirements, and also as an alternative source of platform chemicals for the chemical industry.<sup>1-4</sup> Of these, inedible lignocellulose residues offers a low cost and abundant source of materials capable of providing a rich diversity of chemical entities which fulfill these requirements.<sup>5-8</sup> In parallel to these developments, the rapid growth in the production of biodiesel has led to a surfeit of glycerol, produced as a by-product of biodiesel manufacture, that is also a potentially important and versatile platform chemical. It is not surprising that glycerol valorisation has also attracted great interest from within the scientific community, and considerable efforts have led to the development of strategies for the conversion of glycerol into products with a diverse range of applications.<sup>9-13</sup> One such approach is the formation of acetals derived from glycerol and bio-mass derived carbonyl compounds, such as furaldehyde, which have found promising application as fuel additives. While routes for the conversion of related furanic materials for use as biofuels are well established,<sup>14-16</sup> similar routes for the valorization of furfural as a platform for biofuel production are less well established.<sup>17-20</sup>

Our interest in this area stems from the potential limitations encountered in the direct acetalization reactions of furaldehyde with alcohols and polyols. Furaldehyde is highly sensitive to polymerisation under the conditions typically encountered in acetal formation, that is, highly acidic environments, high temperatures and extended reaction times.<sup>21,22</sup> Furthermore, acetalization protocols generally require a method of removing the water generated in the course of the acetalization reaction to shift the equilibrium in favour of the acetal product and, in the case of water sensitive catalysts, to avoid catalyst degradation. This is achieved either by a number of methods such as the inclusion of a sacrificial dehydrating agent or by physical removal of the water, for example, by aspiration with a stream of gas or the use of a Dean-

Stark apparatus.<sup>23–27</sup> While effective, these approaches are inefficient both in terms of energy requirements necessitating high temperatures which also contribute to furaldehyde degradation and impact negatively on overall atom efficiency. In addition, the direct acetalization of glycerol with carbonyl compounds can be limited by the poor solubility of reagents in glycerol which leads to mass transfer issues. Thus, the synthesis of cyclic furaldehyde acetals would appear to be best suited to a transacetalization approach which is thermodynamically and kinetically favoured over the direct acetalization strategy<sup>28</sup> and so might allow for the development of more benign and operationally simple reaction protocols. Transacetalization of acyclic acetals has previously been demonstrated to be a highly effective strategy to circumvent the low yields of cyclic acetal products obtained from unreactive carbonyl compounds, and to improve selectivity in the case of substrates bearing multiple functional groups.<sup>28–31</sup>

We have previously demonstrated that mildly acidic nanoporous aluminosilicate materials, produced by an operationally simple evaporation induced self-assembly (EISA) approach,<sup>32–36</sup> are highly effective catalysts for the formation of acyclic acetals directly from carbonyl compounds and short chain alcohols without the requirement for additional dehydrating agents.<sup>37–39</sup> Furthermore, their acidic characteristics are also highly suited to catalyze transacetalization reactions of acyclic acetals to the corresponding cyclic acetals.<sup>40</sup> We reasoned therefore that it should be possible to combine these two reactions to develop an operationally simple and efficient telescoped protocol which would avoid the requirement to employ separate acetalization/transacetalization protocols, and the requirement to isolate and purify sensitive products (**Scheme 1**). Ideally, this protocol would employ only mildly acidic conditions, short reaction times and moderate reaction temperatures to limit furaldehyde decomposition commonly observed in acetalization reactions.<sup>23</sup>



**Scheme 1: Telescoped Routes to Glycerol Acetals**

Herein we report our initial studies for the development of such a telescoped reaction protocol in which the acyclic acetal is generated *in situ* before undergoing transacetalization with glycerol to produce acyclic acetal products in short reaction times and under mild reaction conditions.

## EXPERIMENTAL SECTION

### General Methods

Purified furaldehyde refers to material obtained by distillation under reduced pressure which provided a clear material that was stored out of direct light. Crude furaldehyde refers to material used as received (see **Supplementary Information**). Methanol and anhydrous 1-propanol, dimethyl carbonate, dimethoxypropane and glycerol were used as received. Nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz in CDCl<sub>3</sub> at 20 °C. The nanoporous materials employed here were prepared using an evaporation induced self-assembly (EISA) approach (see **Supplementary Information**) or as described previously.<sup>33–37,39,40</sup>

### Synthesis of Furaldehyde Dimethyl Acetal (2a) Employing Nanoporous Aluminosilicate Catalysts

The Al-13-(3.18) catalyst (40 mg) was added to a solution of crude furaldehyde (96mg, 1 mmol) in methanol (2 mL) and the reaction heated to 60 °C for 1 hour. On completion of the reaction, a sample of the reaction mixture was withdrawn and filtered through a Celite plug to remove the catalyst. The plug was washed with deuterated chloroform (2 × 0.25 mL) and the crude reaction mixture was analysed by quantitative <sup>1</sup>H NMR analysis employing *para*-xylene as an internal standard.

## Telescoped Reaction for the Formation of Glycerol Acetal Products

The Al-13-(3.18) catalyst (40 mg) was added to a solution of crude furaldehyde (384mg, 4 mmol) and glycerol (92 mg, 1 mmol) in dimethyl carbonate (2 mL) and 1-propanol (300 mg, 5 mmol) and the reaction heated to 80 °C for 1 hour. On completion of the reaction, a sample of the reaction mixture was withdrawn and filtered through a Celite plug to remove the catalyst. The plug was washed with deuterated chloroform (2 × 0.25 mL) and the crude reaction mixture was analysed by quantitative <sup>1</sup>H NMR analysis employing *para*-xylene as an internal standard.

## RESULTS AND DISCUSSION

Our previous studies have demonstrated that the nanoporous aluminosilicate materials Al-13-(2.42) and Al-13-(3.18) displaying a Si/Al ratio of 13:1 (see **Supplementary Information**) are highly effective catalysts for both acetal formation and acetal exchange reactions. Our initial work therefore investigated the ability of these aluminosilicate materials (**Table 1**) to catalyze the formation of the corresponding acyclic dimethyl acetal **2a** from furaldehyde, employing methanol as the acetalization reagent.

**Table 1: Nanoporous Silicate Physical Properties.**

Catalyst <sup>a</sup>	M:Al:Si Gel Composition	BET Surface Area (m <sup>2</sup> g <sup>-1</sup> ) <sup>b</sup>	Acidity (μmol g <sup>-1</sup> ) <sup>c</sup>	Pore Width (nm) <sup>d</sup>
Al-13-(2.34)	0:1:13	614	440	2.34
Al-13-(3.18)	0:1:13	980	530	3.18
B-13-(3.54)	1:0:13	1095	590	3.54
B-13-(2.34)	1:0:13	797	330	2.34
B-Al-13-(2.20)	1:1:13	569	590	2.20
Ce-Al-13-(2.60)	1:1:13	342	ND	2.60
Zr-Al-13-(2.13)	1:1:13	280	ND	2.13

<sup>a</sup> M/Al/Si gel ratio with pore size in parenthesis.

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

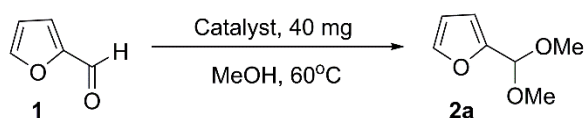
<sup>c</sup> Determined by temperature programmed desorption (TPD) analysis.

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

We envisaged that **2a** might serve as a suitable precursor for the subsequent acetal exchange reaction with glycerol to provide the corresponding cyclic acetals and allow for the development of a telescoped route in which the acyclic acetal is generated *in situ* and so does not require isolation. Telescoped reaction strategies have proven to be a highly attractive approach given the potential savings in time and efficiency afforded by reducing the number of isolation and purification steps and this approach has found widespread use in synthetic chemistry especially where products are unstable, highly reactive or are difficult to isolate.<sup>41-46</sup>

In line with our previous studies, both aluminosilicate materials Al-13-(2.42) and Al-13-(3.18) efficiently catalyzed the formation of **2a** from distilled furaldehyde in methanol in short reaction times under mild reaction conditions (**Table 2**, entries 2 and 3).<sup>37,38</sup>

**Table 2: Optimisation of Furaldehyde Dimethylacetal Formation<sup>a</sup>**



Entry	Catalyst	Solvent	Acetal	Time (h)	Yield <b>2a</b> (%) <sup>b</sup>
1	No Catalyst	MeOH	-	1	10 <sup>c</sup>
2	Al-13-(2.42)	MeOH	-	1	75 <sup>c</sup>
3	Al-13-(3.18)	MeOH	-	1	75 <sup>c</sup>
4	Al-13-(2.42)	MeOH	-	1	72
5	Al-13-(3.18)	MeOH	-	1	71
6	B-13-(3.54)	MeOH	-	1	63
7	B-13-(2.43)	MeOH	-	1	54
8	B-Al-13-(2.20)	MeOH	-	1	62
9	Ce-Al-13-(3.18)	MeOH	-	1	64
10	Zr-Al-13-(3.18)	MeOH	-	1	76
11	Al-13-(2.42)	DMC	DMOP	2	18 <sup>d</sup>
12	Al-13-(3.18)	DMC	DMOP	2	34 <sup>d</sup>

<sup>a</sup> Experimental: The catalyst (40 mg) was added to a solution of crude furaldehyde (96 mg, 1 mmol) in methanol (2 mL) and the reaction heated to 60 °C for 1 hour.

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

<sup>c</sup> Reaction employing distilled furaldehyde.

<sup>d</sup> Reaction in dimethyl carbonate (DMC).

We were also interested, however, in the possibility of employing crude furaldehyde and so further improve the efficiency of this approach by developing a route that was not reliant on using purified starting

material. Gratifyingly, little difference in overall yields were observed on employing crude furaldehyde in these reactions (entries 4 and 5).

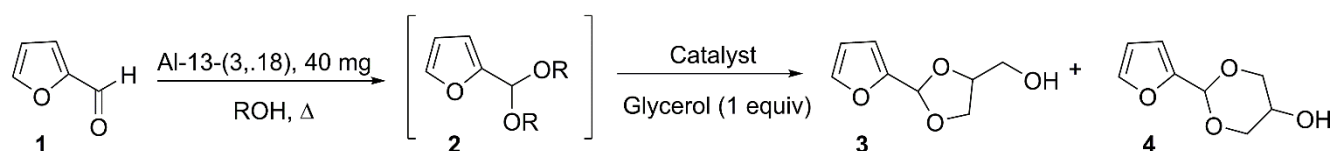
We next investigated the role of the catalyst, and whether overall yields **2a** were strongly affected by the Lewis acid or Brønsted acid properties of the catalyst. It has been reported that a combination of strong Lewis acid sites and an excess of Brønsted acid sites provides an ideal combination for high conversions of carbonyl compounds to acetal products using short chain alcohols.<sup>47</sup> We were intrigued as to whether a similar effect could be achieved here, and so we next studied a selection of nanoporous silicate materials displaying either predominantly Lewis acidity (B-13-(2.43) and B-13-(3.54)),<sup>48</sup> in addition to aluminosilicate materials containing metals demonstrated to exhibit both Lewis and Brønsted acidity (B-Al-13-(2.20), Ce-Al-13-(2.60) and Zr-Al-13-(2.13)).<sup>49-51</sup> The Lewis acid catalysts B-13-(3.54) and B-13-(2.43) displayed moderate catalytic activity (entries 6 and 7), which was comparable to the performance of the B-Al-13-(2.20) and Ce-Al-13-(2.60) material (entries 8 and 9). The zirconia/alumina material Zr-Al-13-(2.13) performed best of these mixed metal catalysts producing similar yields to the aluminosilicate materials (entry 10). Finally, we also took the opportunity to confirm the potential for employing an acetal exchange approach using these catalysts employing the acyclic ketal dimethoxy propane (DMOP) as the acetalization reagent in dimethyl carbonate (DMC). Both of the aluminosilicate catalysts provided **2a** in moderate yields under similar reaction conditions, albeit employing stoichiometric quantities of DMOP (entries 11 and 12).

With effective methodology for the preparation of **2a** in hand, we next investigated conditions for the development of the telescoped reaction protocol employing the Al-13-(3.18) catalyst. Our initial reactions carried out in methanol with stoichiometric quantities of glycerol provided high conversions of furaldehyde to the corresponding dimethyl acetal **2a**, however, the subsequent transacetalization reaction proved to be sluggish providing only small amounts of the dioxane and dioxolane products **3** and **4** which were not improved by increasing the reaction temperature (**Table 3**, entries 1–3). We reasoned that the low yields observed were due in part to the high nucleophilicity of methanol coupled with the large excess



present in the reaction which was detrimental to transacetalization. We therefore next investigated the telescoped protocol in dimethyl carbonate,<sup>52</sup> employing only a small excess (5 equivalents) of methanol. Reactions in dimethyl carbonate with no methanol present provided low yields of **3** and **4** (entry 4), however, we were highly gratified to observe that on the addition of methanol, significant conversions to cyclic acetal products were achieved with reasonable selectivity for the acetal products (entry 5) which were improved on increasing the reaction temperature (entries 6–8). We reasoned that further improvements in overall yields of dioxane and dioxolane products might be realised by switching to a less nucleophilic alcohol, and indeed, employing 1-propanol in place of methanol provided acceptable yields of **3** and **4** with excellent selectivity for the cyclic acetal products (entries 9 and 10).

**Table 3: Optimisation of Telescoped Protocol for Glycerol Acetalization**



Entry	Solvent	Time (h)	Temp (°C)	ROH (5 equiv)	Conversion (%)	Ratio 3:4 (%)	Yield 3+4 (%) <sup>b</sup>	Mass Balance (%) <sup>c</sup>
1	MeOH	2	60	-	68	60:40	20 <sup>d</sup>	98
2	MeOH	2	60	-	74	57:43	20	94
3	MeOH	1	80	-	68	55:45	18	94
4	DMC	2	60	-	18	67:33	18	98
5	DMC	2	60	MeOH	40	64:36	32	94
6	DMC	1	80	-	24	67:33	24	94
7	DMC	1	80	MeOH	48	68:32	44	98
8	DMC	2	80	MeOH	48	70:30	42	96
9	DMC	1	80	PrOH	52	71:29	50	98
10	DMC	2	80	PrOH	54	68:32	52	96
11	DMC	2	80	PrOH	54	68:32	52 <sup>e</sup>	98
12	PrOH	2	80	-	44	64:36	26 <sup>e</sup>	98

<sup>a</sup> Experimental: The catalyst (40 mg) was added to a solution of crude furaldehyde (96 mg, 1 mmol) in the specified solvent (2 mL) and heated to the specified temperature for the specified time.

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

<sup>c</sup> Sum of acetal products and furaldehyde determined by <sup>1</sup>H NMR analysis of the crude reaction.

<sup>d</sup> Reaction employing distilled furaldehyde.

<sup>e</sup> Reaction employing 75 mg of catalyst,

In line with previous literature reports, increasing the amount of catalyst had little effect (entry 11).<sup>25</sup>

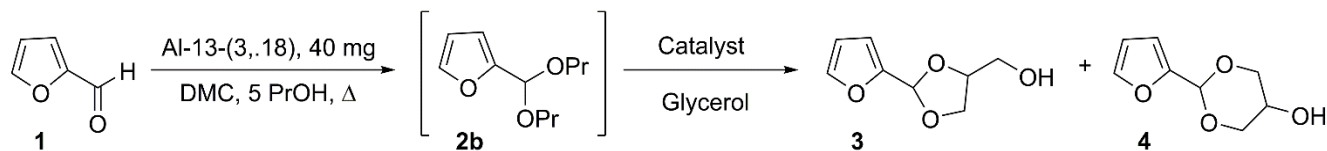
Carrying out the reaction in 1-propanol as the solvent provided only moderate overall conversions

producing significant quantities of the acyclic dipropyl acetal **2b** and hence poor selectivity for the cyclic acetal products (entry 12). In all cases, ratios of dioxane and dioxolane product ratios were similar to previous literature reports consisting of approximately 2:1 quantities of the four possible conformational isomers (*trans*)-**3**, (*cis*)-**3**, (*trans*)-**4** and (*cis*)-**4**,<sup>23,25</sup> and reflects the existence of a temperature-dependent acid catalyzed equilibrium.<sup>53</sup> Mass balances for these reactions were calculated from <sup>1</sup>H NMR reactions and indicated that very little insoluble polymeric materials were formed under the reaction conditions. We next investigated whether modification of the Lewis acid/Bronsted acid characteristics of the catalyst played a significant role in determining catalyst activity and product ratios. Disappointingly, nanoporous borosilicate materials or aluminosilicate materials containing boron, cerium or zirconium performed poorly under our standard conditions, with only the zirconium containing aluminosilicate material Zr-Al-Si-(2.13) displayed significant catalytic activity (**Supplementary Information, Table S1**).

Finally, we completed our optimisation studies by investigating the effect of changing the stoichiometry of the reaction components. Previous studies in this area have demonstrated that high conversions to cyclic acetals are achieved by using an excess of either furaldehyde or glycerol. Given the propensity of heterogeneous catalysts to aggregate at high glycerol loadings,<sup>33</sup> we investigated the effect of increasing quantities of furaldehyde (**Table 4**). Direct acetalization of furaldehyde with glycerol proceeded efficiently in the absence of 1-propanol under our standard reaction conditions to provide moderate overall yields of **3** and **4** in short reaction times (entry 1). As previously, however, overall yields of **3** and **4** were significantly increased in the presence of a small excess of 1-propanol (entry 2). Similarly, further increasing the amount of furaldehyde to four equivalents provided additional improvements, and under these conditions, excellent yields of cyclic acetal products were obtained (entries 3–4). We have previously demonstrated that these nanoporous aluminosilicate materials are fully recyclable and reusable, and indeed, similar yields of acetal products were achieved from reactions employing catalyst that had been isolated from reaction mixtures and recalined (entry 5).<sup>34</sup> Additional benefits of using an excess of

furaldehyde were also evident on the reaction temperature and allowed high yields of acetal products to be obtained even at 60 °C albeit with slightly extended reaction times (entries 6 and 7).

**Table 4: Reaction Optimisation and Catalyst Recycling**



Entry	Solvent	Furaldehyde (equiv)	ROH (5 equiv)	Conversion (%)	Ratio 3:4 (%)	Yield 3 + 4 (%) <sup>b</sup>	Mass Balance (%)
1	DMC	2	-	50	68:32	50	94
2	DMC	2	PrOH	76	69:31	70	98
3	DMC	4	-	58	69:31	58	96
4	DMC	4	PrOH	88	68:32	80	96
5	DMC	4	PrOH	88	67:33	84 <sup>c</sup>	96
6	DMC	4	-	30	65:35	30 <sup>d</sup>	92
7	DMC	4	PrOH	64	62:38	60 <sup>d</sup>	98
8	DMC	4	PrOH	48	70:30	40 <sup>e</sup>	93

<sup>a</sup> Experimental: The catalyst (40 mg) was added to a solution of crude furaldehyde in the specified solvent (2 mL) and the reaction heated to the specified temperature for 1 hour.

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

<sup>c</sup> Reaction employing recycled/recalcined catalyst

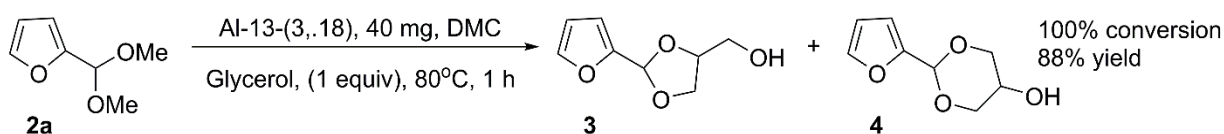
<sup>d</sup> Reaction at 60 °C.

<sup>e</sup> Reaction using B-13-(3.54)

Furthermore, significant improvements in overall yields were now also observed with catalysts that were effectively inactive under stoichiometric conditions, for example, with the boron containing catalyst B-13-(3.54) (Supplementary Information, Table S1).

Our final studies investigated whether the enhanced yields of acetal products observed in reactions containing methanol and 1-propanol do indeed result from a transacetalization reaction of the acyclic acetal intermediate, rather than enhanced dispersion of the catalyst in the presence of a polar co-solvent. We have previously observed that aluminosilicate materials have a tendency to aggregate in glycerol containing reactions in non-polar solvents leading to poor dispersion of the catalyst in the reaction medium.<sup>33</sup> With this in mind, we synthesized and isolated an authentic sample of **2a**, and reacted it in the presence of glycerol and Al-13-(3.18) in DMC under our standard reaction conditions. Gratifyingly, the

dimethyl acetal underwent smooth conversion to provide only the dioxane and dioxolane products **3** and **4** in excellent yield (**Scheme 2**).



**Scheme 2: Transacetalization Reaction of Furaldehyde Dimethyl Acetal 2a**

## CONCLUSIONS

In conclusion, we have demonstrated that mildly acidic nanoporous aluminosilicate materials efficiently produce acetal products from either pure or crude furaldehyde at low catalyst loadings in the presence of alcohols and polyols, such as glycerol. In the case of glycerol, yields can be further improved by the addition of a small excess of short chain alcohols, such as methanol or 1-propanol, allowing for the development of a telescoped acetalization/transacetalization protocol in which the acyclic acetal is initially generated *in situ* and undergoes subsequent transacetalization in the presence of glycerol to produce the corresponding dioxane and dioxolane products in high yields. Importantly, these telescoped reaction protocols proceed efficiently employing crude furaldehyde and so is not reliant on using purified material. They proceed at moderate reaction temperatures employing catalysts displaying moderate acidity and hence the formation of the insoluble polymeric materials typically observed in acetalization processes is minimal. In contrast to previous literature examples, these reactions are operationally simple and do not employ any additional measures, such as the requirement to use an inert atmosphere or a continuous stream of dry nitrogen over the reaction to remove water in order to achieve high yields of acetal products or distillation conditions employing Dean-Stark conditions to remove the more volatile alcohol. The reaction employs a fully recyclable catalyst and proceeds efficiently in short reaction times to give high yields of cyclic acetal products which do not require prolonged heating at high temperatures.

## **ASSOCIATED CONTENT**

### **Supplementary Information**

General methods, experimental procedures, catalyst characterization techniques, optimization studies and <sup>1</sup>H NMR and GC–MS data for acetal products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## **ACKNOWLEDGEMENTS**

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## **Notes**

The authors declare no competing financial interest.

## REFERENCES

- (1) Huber, G. W.; Iborra, S.; Corma, A. Synthesis of transportation fuels from biomass: chemistry, catalysis and engineering. *Chem. Rev.* **2006**, *106* (9), 4044–4098. DOI: 10.1021/cr068360d
- (2) Zhou, C.-H.; Beltramini, J. N.; Fan Y.-X.; Lu, G. Q. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. *Chem. Soc. Rev.* **2008**, *37* (3), 527–549. DOI: 10.1039/b707343g
- (3) Corma, A.; Iborra, S.; Vely, A. Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* **2007**, *107* (6), 2411–2502. DOI: 10.1021/cr050989d
- (4) Sheldon, R. The road to biorenewables: carbohydrates to commodity chemicals. *ACS Sustain. Chem. Eng.* **2018**, *6* (4), 4464–4480. DOI: 10.1021/acssuschemeng.8b00376
- (5) Delidovich, I.; Hausoul, P. J. C.; Deng, Li.; Pfützenreuter, R.; Rose M.; Palkovits, R. Alternative monomers based on lignocellulose and their use for polymer production. *Chem. Rev.* **2016**, *116* (3), 1540–1599. DOI: 10.1021/acs.chemrev.5b00354
- (6) Gallezot, P. Conversion of biomass to selected chemical products. *Chem. Soc. Rev.* **2012**, *41* (4), 1538–1558. DOI: 10.1039/c1cs15147a
- (7) Hayes, D. J.; Fitzpatrick, S.; Hayes, M. H. B.; Ross, J. R. H. The Biofine Process – Production of Levulinic Acid, Furfural, and Formic Acid from Lignocellulosic Feedstocks. In *Biorefineries-Industrial Processes and Products: Status Quo and Future Directions*; ed. Kamm, B.; Gruber P. R.; Kamm, M., Eds.; Wiley-VCH, Weinheim, 2008.
- (8) Lui, M. Y.; Yuet, C.; Won, Y.; Choi, A. W-T.; Mui, Y. F.; Qi, L.; Horváth, I. T. Valorization of carbohydrates of agricultural residues and food wastes: a key strategy for carbon conservation. *ACS Sustain. Chem. Eng.* **2019**, *7* (21), 17799–17807. DOI: 10.1021/acssuschemeng.9b04242
- (9) Pagliaro, M.; Cirimuina, R.; Kimura, H.; Rossi, M.; Pina, C. D. From glycerol to value added products. *Angew. Chem. Int. Ed.* **2007**, *46* (24), 4434–4440. DOI: 10.1002/anie.200604694

- (10) Zhou, C.-H.; Beltramini, J. N.; Fan Y.-X.; Lu, G. Q. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. *Chem. Soc. Rev.* **2008**, *37* (3), 527–549. DOI: 10.1039/b707343g
- (11) Izquierdo J. F.; Montiel, M.; Palés, I.; Outón, P. R.; Galán, M.; Jutglar, L.; Villarrubia, M.; Izquierdo, M.; Hermo, M. P.; Ariza X. Fuel additives from glycerol etherification with light olefins: state of the art. *Renew. Sustain. Energy Rev.* **2012**, *16* (9), 6717–6724. DOI: 10.1016/j.rser.2012.08.005
- (12) Anitha, M.; Kamarudin, S. K.; Kofli, N. T. The potential of glycerol as a value-added commodity. *Chem. Eng. J.* **2016**, *295*, 119–130. DOI: 10.1016/j.cej.2016.03.012
- (13) Kaur, J.; Sarma, A. K.; Jha, M. K.; Gera, P. Valorisation of crude glycerol to value-added products: Perspectives of process technology, economics and environmental issues. *Biotech. Rep.* **2020**, *27*, e00487. DOI: 10.1016/j.btre.2020.e00487
- (14) Lange, J.-P.; Price, R.; Ayoub, P. M.; Louis, J.; Petrus, L.; Clarke L.; Gosselink, H. Valeric biofuels: a platform of cellulosic transportation fuels. *Angew. Chem. Int. Ed.* **2010**, *49* (26), 4479–4483. DOI: 10.1002/anie.201000655
- (15) Chaffey, D. R.; Bere, T.; Davies, T. E.; Apperley, D. C.; Taylor, S. H.; Graham, A. E. Conversion of levulinic acid to levulinate ester biofuels by heterogeneous catalysts in the presence of acetals and ketals. *Appl. Catal. B* **2021**, *293*, 120219. DOI: 10.1016/j.apcatb.2021.120219
- (16) Lange, J.-P. van der Graaf, W. D.; Haan, R. J.; Conversion of furfuryl alcohol into ethyl levulinate using solid acid catalysts. *ChemSusChem* **2009**, *2* (5), 437–431. DOI: 10.1002/cssc.200800216
- (17) Bohre, A.; Dutta, S.; Saha, B.; Abu-Omar, M. M. Upgrading furfurals to drop-in biofuels: an overview. *ACS Sustain. Chem. Eng.* **2015**, *3* (7), 1263–1277. DOI: 10.1021/acssuschemeng.5b00271
- (18) Dutta, S.; De, S.; Saha, B.; Alam, M. I. Advances in conversion of hemicellulosic biomass to furfural and upgrading to biofuels. *Catal. Sci. Technol.* **2012**, *2* (10), 2025–2036. DOI: 10.1039/c2cy20235b

- (19) Lange, J.-P.; van der Heide, E.; van Buijtenen, J.; Price, R. Furfural- A promising platform for lignocellulosic biofuels. *ChemSusChem* **2012**, *5* (1), 150–166. DOI: 10.1002/cssc.201100648
- (20) Kean, J. R.; Graham, A. E. Indium (III) triflate promoted synthesis of alkyl levulinates from furfuryl alcohols and furfuryl aldehydes. *Catal. Commun.* **2015**, *59*, 175–179. DOI: 10.1016/j.catcom.2014.10.013
- (21) Lamminpää, K.; Ahola, J.; Tanskanen, J. Kinetics of furfural destruction in a formic acid medium. *RSC Adv.* **2014**, *4* (104), 60243–60248. DOI: 10.1039/c4ra09276g
- (22) Williams, D. L.; Dunlop, A. P. Kinetics of furfural destruction in acidic aqueous media. *Ind. Eng. Chem.* **1948**, *40* (2), 239–241. DOI: 10.1021/ie50458a012
- (23) Wegenhart, B. L.; Liu, S.; Thom, M.; Stanley, D.; Abu-Omar, M. M. Solvent-free methods for making acetals derived from glycerol and furfural and their use as a biodiesel fuel component. *ACS Catal.* **2012**, *2* (12), 2524–2530. DOI: 10.1021/cs300562e
- (24) Arias, K. S.; Garcia-Ortiz, A.; Climent, M. J.; Corma, A.; Iborra, S. Mutual valorization of 5-hydroxymethylfurfural and glycerol into valuable diol monomers with solid acid catalysts. *ACS Sustain. Chem. Eng.* **2018**, *6* (3), 4239–4245. DOI: 10.1021/acssuschemeng.7b04685
- (25) Gonzalez-Arellano, C.; Arancon, R. A. D.; Luque, R. Al-SBA-15 catalysed cross-esterification and acetalisation of biomass-derived platform chemicals. *Green Chem.* **2014**, *16* (12), 4985–4993. DOI: 10.1039/c4gc01105h
- (26) Konwar, L. J.; Samikannu, A.; Mäki-Arvela, P.; Boström, D.; Mikkola, J.-P. Lignosulfonate-based macro/mesoporous solid protonic acids for acetalization of glycerol to bio-additives. *Appl. Catal. B* **2018**, *220*, 314–323. DOI: 10.1016/j.apcatb.2017.08.061
- (27) Akinnawo, C. A.; Mosia, L.; Alimi, O. A.; Oseghale, C. O.; Fapojuwo, D. P.; Bingwa, N.; Meijboom, R. Eco-friendly synthesis of valuable fuel bio-additives from glycerol. *Catal. Commun.* **2021**, *152*, 106287–106292. DOI: 10.1016/j.catcom.2021.106287



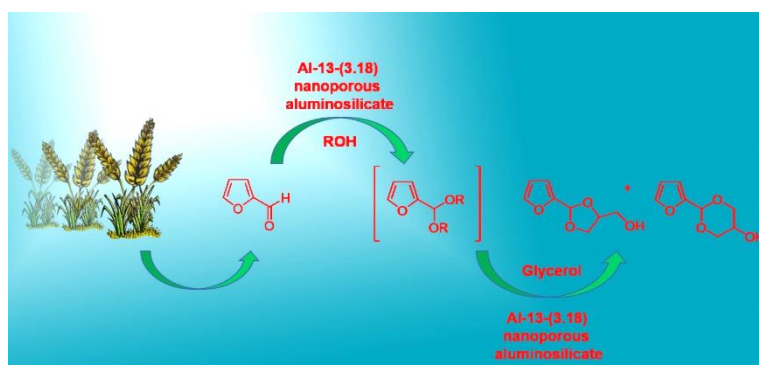
- (28) Arias, K. S; Al-Resayes, S. I.; Climent, M. J.; Corma, A.; Iborra, S. From biomass to chemicals: synthesis of precursors of biodegradable surfactants from 5-hydroxymethylfurfural. *ChemSusChem* **2013**, *6* (1), 123–131. DOI: 10.1002/cssc.201200513
- (29) Smith, B. M.; Kubczyk, T. M.; Graham, A. E. Indium (III) triflate catalysed transacetalisation reactions of diols and triols under solvent-free conditions. *Tetrahedron* **2012**, *68* (38), 7775–7781. DOI: 10.1016/j.tet.2012.07.048
- (30) Smith, B. M.; Kubczyk, T. M.; Graham, A. E. Metal triflate catalysed acetal exchange reactions of glycerol under solvent-free conditions. *RSC Adv.* **2012**, *2* (7), 2702–2706. DOI: 10.1039/c2ra20100c
- (31) Smith, B. M.; Graham, A. E. Indium triflate mediated tandem acetalization-acetal exchange reactions under solvent-free conditions. *Tetrahedron Lett.* **2011**, *52* (47), 6281–6283. DOI: 10.1016/j.tetlet.2011.09.087
- (32) Chaffey, D. R.; Davies, T. E.; Taylor S. H.; Graham, A. E. Etherification reactions of furfuryl alcohol in the presence of orthoesters and ketals; Application to the synthesis of furfuryl ether bio-fuels. *ACS Sustain. Chem. Eng.* **2018**, *6* (4), 4996–5002. DOI: 10.1021/acssuschemeng.7b04636
- (33) Davies, T. E.; Kean, J. R.; Apperley, D. C.; Taylor S. H.; Graham, A. E. Dehydrative etherification reactions of glycerol with alcohols catalyzed by recyclable nanoporous aluminosilicates: telescoped routes to glyceryl ethers. *ACS Sustain. Chem. Eng.* **2016**, *4* (3), 835–843. DOI: 10.1021/acssuschemeng.5b00894
- (34) Davies, T. E.; Kean, J. R.; Apperley, D. C.; Taylor S. H.; Graham, A. E. Nanoporous aluminosilicate-mediated synthesis of ethers by a dehydrative etherification approach. *ACS Sustain. Chem. Eng.* **2014**, *2* (4), 860–866. DOI: 10.1021/sc400492x
- (35) Robinson, M. W. C.; Davies, A. M.; Mabbett, I.; Apperley, D. C.; Taylor, S. H.; Graham A. E. Synthesis and catalytic activity of nanoporous aluminosilicate materials. *J. Mol. Catal. A* **2009**, *314* (1-2), 10–14. DOI: 10.1016/j.molcata.2009.09.005
- (36) Robinson, M. W. C.; Davies, A. M.; Mabbett, I.; Apperley, D. C.; Taylor, S. H.; Graham A. E. Synthesis of nanoporous aluminosilicate materials and their application as highly selective

- heterogeneous catalysts for the synthesis of  $\beta$ -amino alcohols. *J. Mol. Catal. A* **2010**, 329 (1-2), 57–63. DOI: 10.1016/j.molcata.2010.06.018
- (37) Davies, T. E.; Taylor S. H.; Graham, A. E. Nanoporous aluminosilicate catalyzed telescoped acetalization-direct aldol reactions of acetals with 1,3-dicarbonyl compounds. *ACS Omega* **2018**, 3 (11), 15482–15491. DOI: 10.1021/acsomega.8b02047
- (38) Robinson, M. W. C.; Graham A. E. Mesoporous aluminosilicate promoted protection and deprotection of carbonyl compounds. *Tetrahedron Lett.* **2007**, 48 (27), 4727–4731. DOI: 10.1016/j.tetlet.2007.05.022
- (39) Kubczyk, Williams, S. M.; Kean, J. R.; T. M.; Davies, T. E.; Taylor S. H.; Graham, A. E. Nanoporous aluminosilicate catalysed Friedel-Crafts alkylation reactions of indoles with aldehydes and acetals. *Green Chem.* **2011**, 13 (9), 2320–2325. DOI: 10.1039/c1gc15669a
- (40) Yip, L.; Kubczyk, T. M.; Davies, T. E.; Taylor, S. H.; Apperley D. C.; Graham, A. E. Nanoporous aluminosilicate mediated transacetalisation reactions: application in glycerol valorization. *Catal. Sci. Tech.* **2012**, 2 (11), 2258–2263. DOI: 10.1039/c2cy20188g
- (41) Hayashi, Y. Pot economy and one-pot synthesis. *Chem. Sci.* **2016**, 7 (2), 866–880. DOI: 10.1039/c5sc02913a
- (42) Phillips, D. J.; Graham, A. E. In situ generation of ylides for tandem oxidation-olefination reactions of unactivated diols. *Synlett* **2008**, 649–652. DOI: 10.1055/s-2008-1042799
- (43) Smith, B. M.; Graham, A. E. Sequential and tandem oxidation/acetalization procedures for the direct generation of acetals from alcohols. *Tetrahedron Lett.* **2007**, 48 (28), 4891–4894. DOI: 10.1016/j.tetlet.2007.05.060
- (44) Phillips, D. J.; Pillinger, K. S.; Wei, L.; Taylor, A. E.; Graham, A. E. Diol desymmetrization as an approach to the synthesis of unsymmetrical dienyl diesters. *Tetrahedron* **2007**, 63 (42), 10528–10533. DOI: 10.1016/j.tet.2007.07.089

- (45) Page, P. C. B.; Graham, A. E.; Park, B. K. A convenient preparation of symmetrical and unsymmetrical 1,2-diketones – application to fluorinated phenytoin synthesis. *Tetrahedron* **1992**, *48* (35), 7265–7274. DOI: 10.1016/S0040-4020(01)88265-X
- (46) Graham, A. E.; Taylor, R. J. K. Synthesis of tricholomenyn A and epi tricholomenyn A by a palladium catalysed  $\beta$ -halo enone coupling route. *J. Chem. Soc. Perkin Trans. 1* **1997**, 1087–1089. DOI: 10.1039/a700980a
- (47) Zhou, B.; Song, F.; Ma, X.; Wang, L. Batch and Continuous-Flow Preparation of Biomass-Derived Furfural Acetals over a TiO<sub>2</sub> Nanoparticle-Exfoliated Montmorillonite Composite Catalyst. *ChemSusChem* **2021**, *14* (11), 2341–2351. DOI: 10.1002/cssc.202100303
- (48) Davies, T. E.; Kondrat, S. A.; Nowika, E.; Kean, J. L.; Harris, C. M.; Socci, J. M.; Apperley, D. C.; Taylor, S. H.; Graham, A. E. Nanoporous alumino- and borosilicate-mediated Meinwald rearrangement of epoxides. *Appl. Catal. A* **2015**, *493*, 17–24. DOI: 10.1016/j.apcata.2014.12.031
- (49) Qin, F.; Wang, Y.; Lu, Y.; Osuga, R.; Gies, H.; Kondo, N. K.; Yokoi, Y. Synthesis of novel aluminoborosilicate isomorphous to zeolite TUN and its acidic and catalytic properties. *Microporous Mesoporous Mater.* **2021**, *323*, 111237. DOI: 10.1016/j.micromeso.2021.111237
- (50) Kalita, P.; Gupta, N. M.; Kumar, R. Synergistic role of acid sites in the Ce-enhanced activity of mesoporous Ce–Al-MCM-41 catalysts in alkylation reactions: FTIR and TPD-ammonia studies. *J. Catal.* **2007**, *245*, 338–347. DOI: 10.1016/j.jcat.2006.10.022
- (51) Melero, J. A.; Morales, G.; Iglesias, J.; Paniagua, M.; López-Aguado, C.; Wilson, K.; Osatiashtiani, A. Efficient one-pot production of  $\gamma$ -valerolactone from xylose over Zr-Al-Beta zeolite: Rational optimization of catalyst synthesis and reaction conditions *Green Chem.* **2017**, *19* (21), 5114–5121. DOI: 10.1039/c7gc01969f
- (52) Ferrer, B.; Alvaro, M.; Garcia H.; Application of Dimethyl Carbonate as Solvent and Reagent. In *Green Solvents 1: Properties and Applications in Chemistry*; Inamuddin, A. M.; Ed.; Springer, 2012.

- (53) Deutsch, J.; Martin, A.; Lieske, H. Investigations on heterogeneously catalysed condensations of glycerol to cyclic acetals. *J. Catal.* **2007**, *245* (2), 428–435. DOI: 10.1016/j.jcat.2006.11.006

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**Synopsis:** Recyclable heterogeneous aluminosilicate materials efficiently catalyze the formation of useful biofuel additives from starting materials derived from waste biomass.