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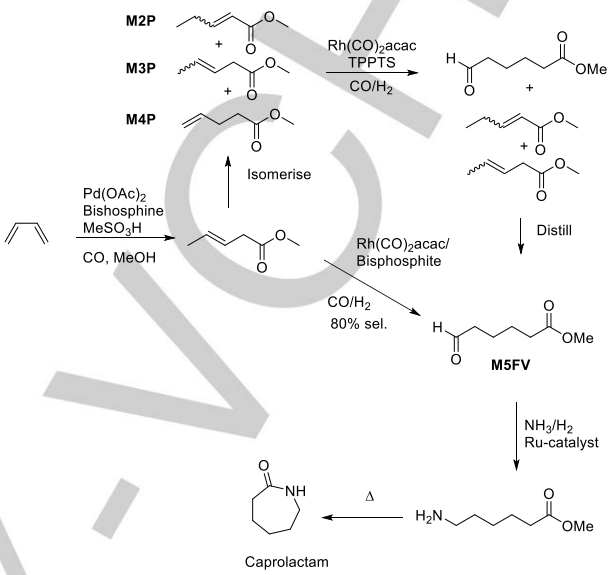
Nylon intermediates from bio-based levulinic acid

Annemarie Marckwordt, Fatima El Ouahabi, Hadis Amani, Sergey Tin, Narayana V. Kalevaru*, Paul C. J. Kamer, Sebastian Wohlrab and Johannes G. de Vries*

Abstract: Use of ZrO_2/SiO_2 as solid acid catalyst in the ring-opening of bio-based γ-valerolactone with methanol in the gas phase leads to mixtures of methyl 2-, 3- and 4-pentenoate (MP) in over 95% selectivity, containing a surprising 81% of M4P. This allows the application of a selective hydroformylation of this mixture in which M4P is converted into methyl 5-formyl-valerate (M5FV) with 90% selectivity and the other isomers remain unreacted. Reductive amination of M5FV and ring-closure to caprolactam in excellent yield had been reported before. The remaining mixture of 2- and 3-MP was subjected to an isomerising methoxycarbonylation to dimethyl adipate in 91% yield.

The production of Nylon-6 has tremendously increased since its discovery in 1938 by Paul Schlack at IG-Farben.[1] The polymer is made by polymerisation of ε-Caprolactam, which is produced by several routes, all starting from benzene.[2] In the 1990s, BASF, DSM and DuPont all worked on synthetic strategies towards caprolactam starting from methyl 3-pentenoate (M3P) obtained by palladium-catalysed methoxycarbonylation of the less expensive butadiene. (Scheme 1).[3] Since M3P has only 5 carbon atoms in the chain, a sixth one had to be added via hydroformylation. This could be done by the isomerising hydroformylation using catalysts based on rhodium with bulky bidentate phosphite ligands that had previously been discovered by Union Carbide for the conversion of butenes to 1-pentanal.[4] Several patents have appeared claiming similar catalysts for this reaction[5] and the best selectivity to methyl 5-formyl-valerate (M5FV) remained at 82%.[5c] Selective hydroformylation of methyl 4-pentenoate (M4P) would have been a lot easier as terminal alkenes are more reactive and can be hydroformylated with very high *n/iso* selectivity, but the isomerisation of M3P gives a mixture of isomers containing at best 4% of M4P.[6] Distillation of this was cumbersome in view of the very close boiling points, which would necessitate the use of extremely high distillation towers and many recycles and for that reason this route was not deemed feasible. Nevertheless, DSM developed a process that allowed the rhodium-catalysed hydroformylation of M4P to M5FV in very high selectivity from a mixture of M3P and M4P, which could be obtained more easily with fewer distillation plates from the isomerization reaction.[7] In this hydroformylation the M3P remained unreacted. M5FV could be easily separated from unreacted M3P by distillation. The effect of the presence of M2P in this reaction was never examined. Reductive amination and ring-closure of the methyl 5-formyl-valerate proceeded in high yield to give caprolactam.[8] This route was never commercialised as the price of butadiene rose again and hence the old routes prevailed.



Scheme 1. Routes to caprolactam from butadiene.

Meanwhile, there is great interest in the production of nylon precursors from renewable resources, not only in view of the dwindling supply of fossil resources, but also because the current production processes for the nylons are associated with a rather high carbon footprint.[9] However, it is possible to bring down the carbon footprint tremendously with a renewables-based process.[10] A good strategy for the conversion of renewable resources to chemicals is based on the use of one of the platform chemicals that were defined in the report made for the DOE of the United States.[11] One of the most promising platform chemicals is levulinic acid (LA) as this C5 building block can be made in a single step from lignocellulose by treatment with dilute sulfuric acid at 200°C.[12] In this process the C6-sugars in the lignocellulose are converted to a 1:1 mixture of levulinic acid and formic acid with over 50% yield. A process was initially developed by Biofine,[13] which however suffered from some shortcomings.[14] In the meantime, an improved process was developed by GFBiochemicals.[15] Once LA is produced on a scale of 100 kTon or more, its price will be lower than most of the currently produced bulk chemicals.

Several catalytic processes have been reported for the hydrogenation of LA to γ-valerolactone (GVL) in excellent selectivities of over 95%.[16] Best catalysts seem to be those based on ruthenium on several different carriers. The use of homogeneous catalysts has also been reported for this conversion with even higher selectivities.[17]

Furthermore, some processes are known for the conversion of GVL / methanol (MeOH) to a mixture containing all 5 possible methyl pentenoates. In this process, the lactone ring-opens to

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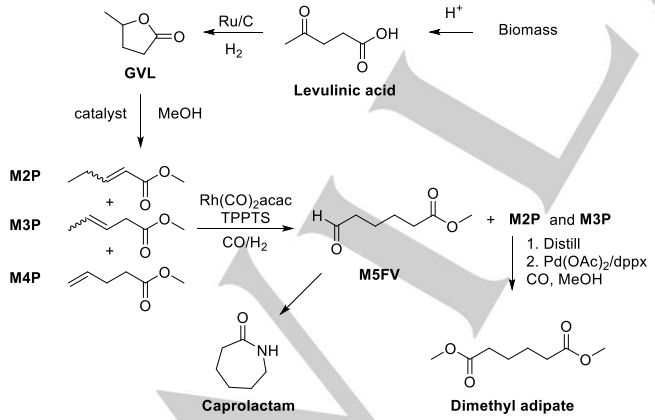
the unsaturated acid and is esterified at the same time. Isomerisation of the double bond also takes place. A number of patents exist on the application of solid acid catalysts.[18] This results in the formation of mixtures in which the relative amount of methyl 4-pentenoate (M4P) is usually below 40%. A liquid phase reactive distillation process has also been reported.[19a] A similar procedure using an acidic ionic liquid gave mainly M3P.[19b] A procedure using basic catalysts in the gas phase is also known.[20] In this latter process the percentage of M4P is usually much higher. However, because of the presence of water that is formed in the reaction, some hydrolysis of the esters takes place, leading to a rapid deactivation of the basic catalyst by the formed acid.

Use of the mixture of pentenoate esters in an isomerising hydroformylation is less attractive because of the presence of relatively large amounts of M2P. The rhodium-alkyl complex formed from this compound by insertion of the alkene into the rhodium hydride complex is relatively stable as a result of the stabilising action of the ester group thus forming an unproductive resting state.[21] Additionally this compound leads to the formation of relatively large amounts of methyl valerate during the hydroformylation.[3b] For this reason, it would be much more attractive to apply the second hydroformylation process developed by DSM. However, this approach will only be economic if a process can be found in which a mixture of methyl pentenoates is formed containing at least 80% of methyl 4-pentenoate based on the use of an acidic catalyst although the remaining pentenoates can be used for the production of adipic acid (Scheme 2).

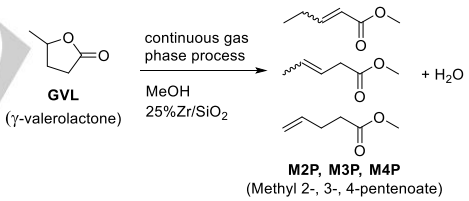
With this background, we started screening a range of solid catalysts in the reaction between GVL and methanol to produce a methyl pentenoate mixture with a high content of M4P (Fig. S5). The ring-opening of GVL to the MP mixture using methanol was initially performed as batch process in an autoclave. From these tests, ZrO_2 supported on SiO_2 was found to be the most active catalyst.



Scheme 2. Route to two nylon precursors starting from bio-based GVL.

However, these batch processes suffered from reproducibility problems. Thus, subsequent experiments were performed as gas phase continuous processes using ZrO_2/SiO_2 as catalysts (Scheme 3). After optimisation of the catalyst composition, the ZrO_2/SiO_2 catalyst with a Zr loading of 25wt% was found to exhibit superior performance compared to other loadings of Zr. Consequently, we have applied this particular composition of 25%ZrO_2/SiO_2 catalyst for the optimisation of the reaction conditions to enhance the selectivity of the terminally unsaturated methyl 4-pentenoate along with high space-time-yields.

The 25%ZrO_2/SiO_2 catalyst was synthesised by wet impregnation and characterised by several techniques such as powder x-ray diffraction (XRD), BET-SA, pore size distribution, temperature programmed desorption of ammonia (NH_3-TPD) and CHN elemental analysis. The XRD pattern of the 25%ZrO_2/SiO_2 catalyst revealed the presence of a ZrO_2 phase besides SiO_2 (Figure S1). However, the diffraction reflections were broad due to small crystallite size (<5 nm). The broadness of the reflections made a clear attribution to either the cubic or tetragonal phase of ZrO_2 difficult. In addition, the presence of a monoclinic ZrO_2 phase could not be excluded. The nitrogen adsorption-desorption isotherm of the catalyst disclosed the type IV isotherm which is typical for mesoporous materials (Figure S2). The mesoporous character of the 25%ZrO_2/SiO_2 catalyst with a pore size of 6.7 nm stemmed from the SiO_2 support. The surface area was found to be 286.5 m^2/g (Table S1). Temperature programmed desorption of ammonia measurements revealed that the 25%ZrO_2/SiO_2 catalyst possesses weak to moderate acid sites with an ammonia uptake of 0.26 mmol g^{-1}. In addition, the catalyst contains basic sites as shown by CO_2 desorption (0.17 mmol CO_2 g^{-1}) (Figure S3 and S4).



Scheme 3. SiO_2 supported ZrO_2-catalysed gas phase reaction GVL to an isomeric mixture of methyl pentenoates enriched in methyl 4-pentenoate.

First, the effect of the reaction temperature on the activity and selectivity was studied. It is obvious from Figure 1a that the product distribution and the GVL conversion are strongly dependent on the reaction temperature. The conversion of GVL is observed to increase from 44% to 85% with increasing temperature from 255 to 315°C and then levelled-off beyond this temperature. The total MP selectivity was found to be very high for all explored temperatures (97 to 99%). At lower temperatures (255 to 295°C) the desired M4P was the major product while M2P was a minor product. With the rise in temperature the selectivity of M2P and M3P is increasing at the expense of M4P. This is presumably due to increased isomerisation of M4P to M3P and M2P because the acid sites of the ZrO_2/SiO_2 catalyst also enhance the isomerisation reaction. The reaction at 295°C shows a good balance in terms of reasonably good M4P selectivity and conversion of GVL.

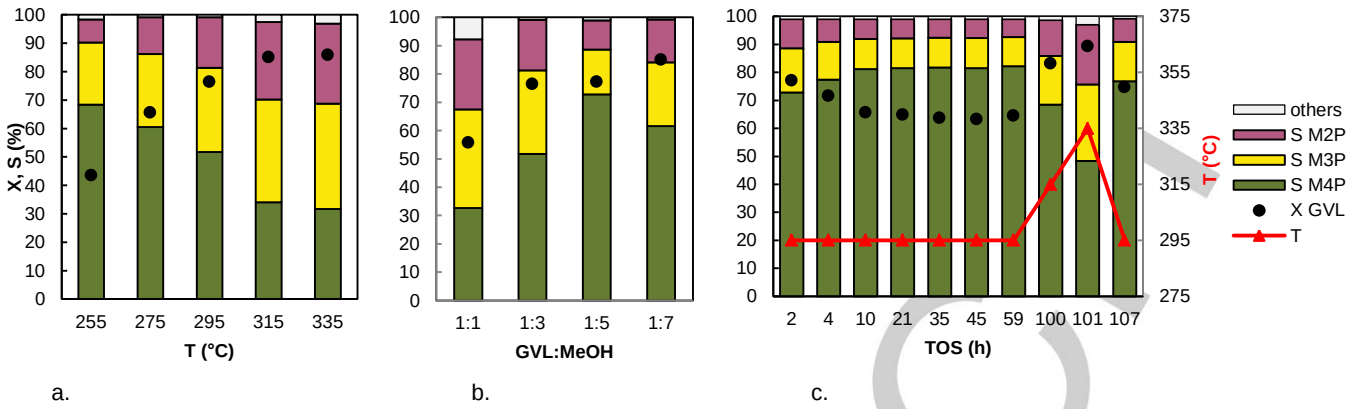
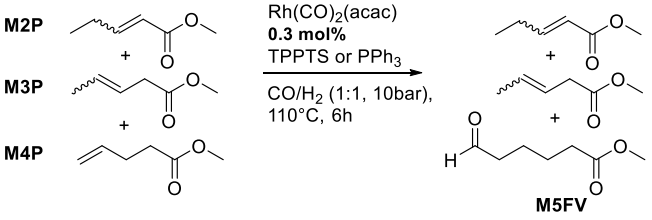


Figure 1. a) Effect of temperature on the transesterification of GVL to MPs using 25%ZrO_2/SiO_2 catalyst (p: 1 bar, GVL 8 mmol/h, GVL : MeOH = 1 : 3, N_2 as carrier gas, total flow 4 l/h, GHSV: 1900 h^{-1}). b) Effect of the GVL : MeOH molar ratio on the transesterification of GVL to MPs using 25%ZrO_2/SiO_2 catalyst (T: 295°C, p: 1 bar, GVL: 8 mmol/h, N_2 as carrier gas, total flow 4 l/h, GHSV: 1900 h^{-1}). c) Long-term stability test over 25%ZrO_2/SiO_2 catalyst (T: 295°C, p: 1 bar, GVL: 8 mmol/h, GVL : MeOH = 1 : 5; N_2 as carrier gas, total flow 4 l/h, GHSV: 1900 h^{-1}).

Next, the influence of the GVL/MeOH molar ratio was investigated. The GVL/MeOH ratio was varied in the range from 1:1 to 1:7 while the total gas flow was kept constant. At 255°C, the GVL conversion was only 34% at the 1:1 molar ratio which increased to 52% at 1:7. Total MP selectivity was found to be ≥97% in all cases. In particular, M4P selectivity improved with increasing GVL/MeOH ratio from 54% (at 1:1 molar ratio) to 78% (at 1:5) and then slightly decreased to 74% (at 1:7) (Figure 1b). In general, the total selectivity of all MP isomers was observed to be 99% at all GVL/MeOH ratios except for the 1:1 molar ratio (92%). Thus, the optimal GVL/MeOH molar ratio in terms of M4P selectivity at a reasonably high conversion of GVL was 1:5.

After optimising the reaction temperature and GVL to MeOH ratios, the long-term stability of the 25%ZrO_2/SiO_2 catalyst was explored under optimised reaction conditions. The idea behind this long-term test was not only to check the catalyst stability but also to collect the MPs product mixture over a longer period of time to allow its use for the hydroformylation reaction to produce nylon precursors. Figure 1c illustrates that the 25%ZrO_2/SiO_2 catalyst displayed consistent performance with excellent long-term stability for a period of ca. 110 h on-stream. The total MP selectivity remained more or less constant at 99% throughout. Nevertheless, during the first 10 h on-stream, a slight deactivation of the catalyst took place and hence the GVL conversion decreased from 77% to 65%, which is however compensated to a certain extent by an increased selectivity to the target M4P. The deactivation is due to organic deposits as evidenced by CHN elemental analysis (S4). The amount of deposits on the spent catalyst after the long-term test was about 2%. The catalyst performance after 10 h on-stream remained more or less stable at about 65% GVL conversion and 81% M4P selectivity. Thus the goal of producing a methyl pentenoate mixture containing >80% methyl 4-pentenoate was successfully achieved. Furthermore, the space-time-yield (STY) of MPs amounts to 620 g/kgCat/h of which M4P is 507 g/kgCat/h. To the best of our knowledge, this is the highest M4P selectivity and STY reported so far for such a long-term test in a gas phase continuous mode. Manzer,[20] and more recently Dumesic et al. also reported very high M4P selectivity from GVL using a basic catalyst.[22] However, they tested the catalyst for only 1 h and no long-term stability was reported. Near the end of the present long-term test, the reaction temperature was first raised to 315°C and then even to 335°C before being returned to 295°C. During the whole time, the reaction was continued by dosing the GVL/MeOH reaction mixture to check the performance of the catalyst after such long hours of testing. The catalyst displayed similar behaviour as observed earlier, the rise in temperature led to an improved GVL conversion while the M4P selectivity decreased. Amazingly, the total MP selectivity did not drop to a considerable extent (i.e. varied from 99 to 97% at 335°C). After returning back to the actual reaction temperature of 295°C again, the product distribution as well as the GVL conversion closely resembled to the initial results. This observation proved that the initial catalyst activity can be restored, if desired, by increasing the temperature even by only 40°C. Furthermore, this can be done while the process is running without any need to shut down the reactor or even stop the reactants dosing. The collected reaction mixture from the long-term test for a period of ca. 110 h was then distilled to obtain the pure mixture of MP isomers.

With the mixture of methyl pentenoates, containing 81% of the terminal pentenoate, 14% of M3P and 5% of M2P in hand (Table1, entry 0), a selective hydroformylation reaction in the presence of $Rh(CO)_2(acac)$ and phosphine ligands under CO/H_2 pressure was performed. The aim of this part of the study is to selectively convert M4P to the terminal aldehyde M5FV, while leaving the remaining pentenoate esters untouched (Scheme 4).



Scheme 4. Rhodium-based selective hydroformylation of methyl 4-pentenoate.

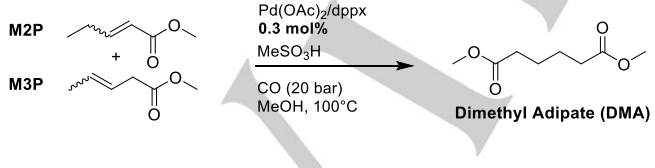
Thus, the mixture was subjected to a biphasic hydroformylation reaction in water/toluene using 0.3 mol% of $Rh(CO)_2acac$ and tri-sulfonated triphenylphosphine (TPPTS) as ligand (L : Rh = 150) at 110°C. M4P was fully converted, achieving 93% selectivity towards formylvalerates (both linear M5FV and branched M4FV) where the l/b ratio was observed to be 97:3 (Table 1, entry 1). In this reaction the amount of M3P increases somewhat, presumably due to isomerisation reactions. When triphenylphosphine (PPh_3) was used as ligand in a single phase reaction in toluene under the same reaction conditions, full conversion of M4P with 100% selectivity towards the formylvalerates was obtained. However, the linear aldehyde M5FV was obtained in only 74% selectivity (Table 1, entry 2). In both examples, the formation of small amounts of the hydrogenated product methyl valerate (MV) was also observed, This is most likely due to hydrogenation of M2P.[3b]

Table 1. Hydroformylation of methyl 4-pentenoate[a]

		Composition (mol%)					Selectivity (%)	
Entry	Ligand	**M4P**	**MFV**	**M3P**	**M2P**	**MV**	**MFV**	l/b
0	-	81	0	14	5	0	-	
1[b]	TPPTS	0	75	19	1	5	93	97/3
2[c]	PPh_3	0	85	9	1	5	100	74/26

[a] 5.7 Mg of $Rh(CO)_2acac$; 0,022 mmol, 6 mmol M4P, 1 mmol M3P, 0.4 mmol M2P, T: 110°C, reaction time: 5 h, p: 10 bar H2/CO (1:1) [b] TPPTS: 1,88 g, 3,3 mmol, 150 eq, in toluene and water as biphasic system. [c] PPh_3: 0,85 mg, 3,3 mmol, 150 eq. in toluene. Conversions and selectivities were calculated by NMR and GC using dodecane as an internal standard.

A facile distillation allowed separation of M5FV from the remaining pentenoate esters.[23] These were subjected to a palladium-catalysed isomerising methoxycarbonylation in the presence of methanol and CO at a pressure of 20 bar (Scheme 5).[24] For this transformation, a catalyst made in situ from $Pd(OAc)_2$ and 1,2-Bis(di-*t*-butylphosphinomethyl)benzene (dppx) was used in order to isomerise the internal alkenes to the terminal position and form the desired dimethyl adipate.[25] Full conversion of the pentenoates and the subsequent isolation of the adipate product in 91% yield was successfully achieved.



Scheme 5. Palladium-catalysed isomerising methoxycarbonylation of methyl 3-pentenoate and methyl 2-pentenoate.

In conclusion, we have been able to achieve over 80% selectivity to the desired M4P from GVL and methanol in a gas phase process using a 25%ZrO_2/SiO_2 catalyst. We assume that this high selectivity to M4P is due to the amphoteric nature of ZrO_2. This may lead to an enzyme-like mechanism in which the acidic sites activate the carbonyl function of the lactone for ring-opening with methanol which is made more nucleophilic by interaction with the weakly basic sites. The GVL/MeOH ratio was found to play a crucial role in both the product distribution and the conversion of GVL. The catalyst displayed excellent long-term stability over a period of ca. 110 h on-stream. Furthermore, we have shown the possibility of producing M5FV with excellent *l/b* selectivity via a highly selective hydroformylation of M4P leaving the other MP isomers mostly untouched. These remaining pentenoates were further valorised by an efficient isomerising methoxycarbonylation which led to the formation of dimethyl adipate in excellent yield. Once levulinic acid is produced on large scale, this route can easily compete with the current fossil-based route.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: homogeneous catalysis • heterogeneous catalysis • γ-valerolactone • methyl pentenoates • nylon

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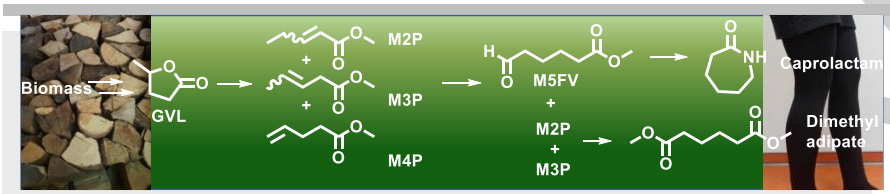

Bio-based Nylon Use of 25% ZrO_2/SiO_2 as catalyst allows the gas phase ring-opening of bio-based γ-valerolactone with methanol to a mixture of methyl pentenoates containing 81% of the 4-isomer, which could be selectively hydroformylated from the mixture to methyl 5-formyl-valerate, an intermediate for caprolactam. The remaining isomers were converted into dimethyl adipate.

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Nylon intermediates from bio-based levulinic acid