

Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201711446 Angew. Chem. 10.1002/ange.201711446

Link to VoR: http://dx.doi.org/10.1002/anie.201711446 http://dx.doi.org/10.1002/ange.201711446

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Catalytic gas-phase production of lactide from renewable alkyl lactates

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Abstract: A new route to lactide, key building block of the bioplastic polylactic acid, is proposed via a continuous catalytic gas-phase transesterification of renewable alkyl lactates in a scalable fixed-bed setup. Supported TiO_2/SiO_2 catalysts are highly selective to lactide, with only minimal lactide racemization. The solvent-free process allows for easy product separation and recycling of unconverted alkyl lactates and recyclable lactyl intermediates. The catalytic activity of TiO_2/SiO_2 catalysts was strongly correlated to their optical properties by DR UV-VIS spectroscopy. Catalysts with high band gap energy of the supported TiO_2 phase, indicative of a high surface spreading of isolated Ti centers, show the highest turnover frequency per Ti site.

The limited accessibility of fossil resources combined with an increased awareness on the environmental impact of traditional petrochemical-derived plastics, exemplified by accumulation of plastic fragments in the environment^[1,2], has driven the search for more sustainable alternatives. In this regard, polylactic acid (PLA) is, among others, considered a benign synthetic substitute, and this bioplastic is already serving in an impressive range of applications.^[3] While life-cycle assessments and comparisons with fossil peer-plastics are positive^[4], current PLA production is expensive, which undermines its significant commercial potential. PLA production today starts with the fermentative production of (usually L-) lactic acid (LA), which is purified by many steps, including an esterification-distillation-hydrolysis procedure.^[5] Significant progress in LA production has been made either by the design of new catalytic routes to LA directly from renewable

feedstocks (sugar, glycerol) or by progress in biotechnology.^[6–8] The industrial route to PLA relies on the intermediate lactide (LD), the cyclic dimer of LA. A controlled ring-opening polymerization (ROP) of LD results in high-molecular-weight PLA chains of relative uniform length. Unfortunately, current LD production is time- and energy-consuming and a major obstacle to cost-friendly PLA. The current two-step LD process runs via a low-molecular-weight prepolymer from L-LA, which is catalytically

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steps are performed at high temperatures under vacuum to aid continuous water or LD removal. These conditions, combined with a moderate L-LD selectivity of 60-70%, mainly due to unwanted racemization of LD and the formation of polymeric waste residue, result in an energy-intensive process that requires strenuous recycling and down-stream purification.^[10,11] Recently, our group proposed a one-step LD route with high yields using shapeselective catalysis.^[12] Here, an aqueous LA solution is mixed with an organic solvent (e.g. xylene) and H-beta zeolite under continuous water removal. This batch process however requires the use of a solvent and continuous energy input by keeping the reactive medium under reflux. A few continuous gas-phase production processes for LD from LA have been proposed earlier, but they are limited by low selectivity, the need for very diluted feeds and vaporization difficulties.^[13–15] As concentrated aqueous LA oligomerizes spontaneously, the LA feed for these processes must be diluted and this entails a large energy cost for the concurrent vaporization of water. Moreover, the initial presence of water is known to catalyze the usually unwanted racemization of LD.^[16] Therefore, we here propose a one-step continuous process for LD production by the transesterification of alkyl lactates in the gas phase in the absence of solvents (Scheme 1, green frame). The incentive to use esters of LA is supported by the fact that they can be fed pure, they are more volatile than the acid (making higher concentrations possible) and they are less prone to autocatalytic side-reactions such dehydration as or

depolymerized again to LD (Scheme 1, blue frame).^[4,9,10] Both



Scheme 1. Schematic overview of the current industrial route to lactide and the gasphase approach presented in this work. PLA production cost breakdown is an estimate of the initial investment cost required for each step.^[30] Note that the catalytic production of MLA also produces D-MLA next to L-MLA, but this stream is not shown for simplicity.



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decarbonylation. Moreover, an ester-based process can be integrated well in the current PLA production scheme, since LA esters are intermediates during the purification of LA, and can be produced catalytically directly from sugars.^[7,17]

More specifically, this contribution shows that catalysts consisting of TiO₂ supported on amorphous SiO₂ (TiO₂/SiO₂) are highly active for the transesterification of L-methyl lactate (MLA) and provide an excellent LD selectivity up to 90%. Under optimized conditions, space time yields (STY) as high as 8 $g_{LD} g_{cat}^{-1} h^{-1}$ can be attained. The remaining product fraction mainly consists of the linear dimer ester methyl lactoyl lactate (ML₂A, 7% selectivity), which can be recycled in the process, providing a total selectivity of 97% towards LD or recyclable intermediates. With only 3% selectivity, the formation of (mostly useful) side-products such as methyl acrylate, methyl pyruvate, methyl-2-methoxy propionate (M₂MP) and acetaldehyde is limited. Racemization is also limited with \leq 7 % of the lactides in *meso* form, compared to common values up to 15 % in patented industrial processes.[10] A conceptual process scheme is proposed in Figure 1. The TiO₂/SiO₂ catalysts are relatively stable over the course of 50 hours, operating slightly below equilibrium at ca. 40% conversion (inset in Figure 1). A minor loss of initial activity is observed, likely due to mild coking (5.6 wt% organic deposits observed by thermogravimetric analysis (TGA) after 50 hours on stream, see Figure S1 in the Supporting Information). The initial activity can be fully restored by in situ regeneration under a flow of 20% O2 in N₂ (Figure S2).

Technically, undiluted L-MLA is vaporized, mixed with N₂ and sent over a fixed catalyst bed containing a 5 wt% TiO₂/SiO₂ catalyst. Offline analysis by ¹H- and ¹³C-NMR spectroscopy of the condensed effluent confirmed the selective nature of the process, with 86% selectivity for LD together with 11% for ML₂A and only 3% for the side-products, mostly M₂MP, at 40% conversion



Figure 1. Conceptual process scheme for the continuous production of LD from L-MLA over a 5wt% TiO₂/SiO₂ catalyst. Reaction conditions: 5.7% L-MLA in N₂, T = 220°C, WHSV = 2.6 h⁻¹, W/F = 2.3 g_{cat} h mol⁻¹. Inset: squares = MLA conversion, triangles, circles and diamonds are the yields of LD, ML₂A and side-products respectively. Note that the separation of some products by a single distillation step might be an oversimplification (e.g. methanol from acetaldehyde), although boiling points are distinct, and a rough indication is found in the ease of GC-separation.

(Figures S3-S6). The slightly lower LD selectivity compared to online analysis might be attributed to partial ring opening of LD with methanol, yielding ML₂A during condensation. The LD fraction consisted of 95% L-LD and 5% meso-LD and no D-LD was observed by chiral GC analysis of the condensate (Figure S7). Due to the large variety in product boiling points (Table S1 in the supporting information) and the absence of solvents, an easy product separation by distillation is anticipated, with recycle of ML₂A and unreacted MLA back to the reactor inlet. Methanol released from the transesterification can be nearly quantitatively recovered as well, for potential reuse in the production of MLA. Indeed, when methanol was used as a substrate instead of MLA, its conversion to dimethylether (DME) was negligible (Figure S8) with TiO₂/SiO₂ catalysts, and only a minor amount (\leq 5%) was lost through the etherification of MLA to M₂MP.

The transesterification of MLA to LD is a thermodynamically restricted equilibrium reaction, as evident from a reaction kinetic profile (Figure 2A, see SI for reaction thermodynamics). Initially, LD is formed at a high selectivity (88-90%), along with a minor fraction of the linear dimer ML₂A (7-9% selectivity). With only 1-2% selectivity, close to no side products are formed. As the reaction reaches equilibrium at ~50% conversion, the formation of side-products slowly increases. The high selectivity towards LD, even at low conversion levels, and the absence of ML₂A build-up suggests that the rate-limiting step is the initial transesterification of two MLA molecules towards ML₂A. At reaction temperatures above 220°C, conversions higher than 50% may be achieved, albeit with a concomitantly decreasing LD selectivity (Figure 2B). At full LD conversion at 300°C, the volatile product fraction consisted nearly entirely of acetaldehyde and methanol (Figures S9-S10). This selectivity decrease could be explained by an irreversible decarbonylation reaction of MLA^[18,19], through equilibrium back-reactions towards the reactant, or by the decarbonylation of LD itself to acetaldehyde and CO (Figure S11).

> Nevertheless, at conversions below 50%, LD selectivity remains high, irrespective of the reaction temperature, and minimal acetaldehyde formation is found at 220°C, (Figure S12). Higher reaction temperatures benefit LD productivity, exemplified by a fourfold increase in STY when working at 280 °C instead of 220 °C (Figure S13). An increase in MLA partial pressure counteracts LD formation according to Le Chatelier's principle, as seen by the corresponding equilibrium product distributions at 220°C (Figure 2C and Figures S14-S15). Nevertheless, higher partial pressures lead to an increased turnover frequency (TOF) and STY, especially when combined with higher temperatures. This way, by using 25% MLA in N₂ and a reactor temperature of 260°C, a STY of 8 g_{LD} g_{cat} h⁻¹ may be obtained, compared to a STY of 1.5 g_{LD} g_{cat} h^{-1} for a standard reaction with 5.7% of MLA in N2 at 220°C (Figure S16). Based on the equilibrium conversions from Figure 2C and the associated vapor compositions (Table S2, not taking the formation of ML₂A or sideproducts into account for simplicity), we





Figure 2. A) Kinetic profile of a reaction of L-MLA to LD using a 5wt% TiO₂/SiO₂ catalyst (5.7% L-MLA in N₂, 220°C). B) Influence of reactor temperature on LD yield and reaction kinetics and corresponding conversion-selectivity plot (inset) (5.7% L-MLA in N₂, 220-300°C). C) Influence of MLA partial pressure on the product distribution at equilibrium (2.3-25.1% L-MLA in N₂, T = 220°C, W/F = 0.19-11.46 g_{cat} h mol⁻¹ depending to reach equilibrium). Values in brackets indicate the % of meso-LD (note that meso-LD amounts are slightly higher at equilibrium). D) DR UV-VIS spectra of TiO₂/SiO₂ catalysts with different wt% of TiO₂ and correlation of corresponding E₀ to the catalyst's TOF (inset: average and standard deviation of three identical runs are plotted, 5.7% L-MLA in N₂, 220°C, WHSV = 15.5 h⁻¹)

estimated the equilibrium constant K_p of the MLA-to-LD reaction to be in the range of 6.3 to 15.3 ×10⁻³ atm at 220°C, corresponding to a Gibbs free energy of reaction (Δ_r G) of about 17 to 21 kJ mol⁻¹ at 220°C (For details, see SI).

While a variety of other metal oxide catalysts also produce LD to some extent (Table S3); supported TiO₂/SiO₂ catalysts are most suitable, particularly in terms of activity, stability and suppression of LD racemization. Transesterification reactions can generally be catalyzed by both basic and acid sites, but bases tend to catalyze LD racemization as well^[20] (e.g. 33% meso-LD with MgO/SiO₂, Table S3). Brønsted acid catalysts (Table 1, entries 2-5) lead to side products (mainly acetaldehyde) in addition to LD, likely due to an increased activity towards MLA decarbonylation.[18] Supported TiO₂/SiO₂ contain almost exclusively Lewis acid sites (see Figure S17 for pyridine-probed IR spectra). This suggests that LD is mainly produced through a Lewis acid-catalyzed mechanism on these catalysts (entry 11). The mixed acidity of SiO₂-Al₂O₃ is responsible for the formation of non-negligible amounts of acetaldehyde at lower conversion levels (entry 4) and substantial amounts of DME (Figure S8). In the absence of catalyst or in the presence of bare SiO₂, no MLA conversion was observed (Table 1, entries 1 & 6), linking all catalytic activity to the supported Lewis acidic TiO₂ phase.

Pure TiO₂ is on the other hand not catalytically active for the MLAto-LD reaction, even when different crystal phases or physical mixtures with SiO₂ were tested (entries 7-10). Clearly, the catalytic performance of the supported TiO₂ active phase is completely modified by interaction with the SiO₂ support.^[21] It is well known that impregnation of SiO₂ with Ti-alkoxides favors the formation of Ti-O-Si bonds over Ti-O-Ti bonds.^[22,23] TiO₂ supported on Si-MCM-41 and a TiO₂-SiO₂ xerogel catalyst also

demonstrate a high LD selectivity (entries 12-13), which suggests that the MLA-to-LD reaction is not structure-sensitive, but that Ti-O-Si bonds between the Ti active sites and a SiO₂ support are indeed important for a high LD selectivity on Ti-based catalysts. Therefore, TiO₂/SiO₂ catalysts with varying wt% of TiO₂ were synthesized and their activities compared for the conversion of MLA to LD (see Table S4 for elemental analysis and N₂-physisorption measurements). No X-ray diffraction patterns assignable to anatase TiO₂ were observed, suggesting the absence of large crystalline TiO₂ particles, even at 30 wt% TiO₂ loadings (Figure S18). Raman spectroscopy, more sensitive to anatase particles^[23], indicated the presence of (few) anatase at 20 wt% (and up) loadings of TiO₂ (Figure S19). The disappearance of the weak band in the SiO₂ support at ~973 cm⁻¹, together with the formation of a new broad band at ~960 cm⁻¹ in the FT-IR spectra of the TiO₂/SiO₂ materials (Figure S20) is indicative of Ti-O-Si bonds.[23]

 Table 1. Gas-phase conversion of L-MLA to LD with various catalysts^[a]

		Selectivity (%)			
Entry	Catalyst	X (%)	LD	ML ₂ A	Other ^[b]
1	No catalyst	0	0	0	0
2	H-beta (Si/Al = 12.5)	48	7	0	93
3	H-beta (Si/Al = 150)	5	60	0	40
4	SiO ₂ -Al ₂ O ₃ ^[c]	20	80	6	14
5	AI-MCM-41 ^[c]	24	49	5	46
6	SiO ₂ support	1	0	0	0
7	TiO ₂ (anatase) ^[c]	32	11	5	84
8	TiO ₂ (rutile) ^[c]	6	0	0	100
9	TiO ₂ (75% anatase/25% rutile) ^[c]	16	0	0	100
10	Physical mixture of TiO2 ^[c] (anatase, 5 wt%) & SiO2 support	4	0	0	100
11	TiO_2/SiO_2 5wt% ^[d] (impregnation)	42	90	8	2
12	TiO ₂ /MCM-41 5wt% ^[d] (impregnation)	46	90	9	1
13	$TiO_2\text{-}SiO_2 \; 5 \; wt\%^{[e]} \; (xerogel)$	39	87	12	1

^[a]Reaction conditions: 5.7% L-MLA in N₂, T = 220°C, WHSV = 3.11 h⁻¹. X = conversion of MLA. ^[b]Other products mainly include M₂MP and acetaldehyde with minor amounts of methyl pyruvate and methyl acrylate. ^[c]Commercial catalysts (see SI). ^[d]Supported catalyst prepared by incipient wetness impregnation. ^[e]xerogel catalyst prepared by sol-gel method. For entries 11-13, 4-5% of all LD is meso-LD.

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DR UV-VIS spectroscopy is a useful tool to provide information on the coordination geometry of the catalytically active Ti cations and ligand environment through the position of ligand to metal charge transfers (LMCT). Such spectra of the dried TiO₂/SiO₂ catalysts are shown in Figure 2D. At low TiO_2 loadings (0.4 – 1 wt%), an LMCT transition band was observed at ~43800 cm⁻¹, commonly attributed to tetrahedral TiO₄ species.^[24,25] For increased TiO₂ loadings, the maximum LMCT transitions red-shift according to an increase in Ti polymerization, suggesting the presence of five-fold TiO₅ or octahedral TiO₆ units in addition to tetrahedral TiO₄ species.^[26] At 20wt% TiO₂, an LMCT transition is observed at ~31000 cm⁻¹, corresponding to octahedral TiO₆ units as in anatase, in agreement with the Raman spectra. The decreasing absorption at 7300 cm⁻¹ in the near-IR region (assigned to the overtone vibration of isolated Si-OH groups) for increasing TiO₂ loadings suggests the gradual coverage of surface Si-OH groups by TiO₂ (Figure S21)^[21]. No vibration absorption related to Ti-OH groups (located at 7156 cm⁻¹) could be observed, possibly due to their instability at temperatures higher than 180°C.[27]

For semiconductor oxides such as TiO₂, the features of the optical absorption edge can give relevant property insights and can for example be used to determine the band gap energy (E_g) (method, see Figure S22).^[28] The value of E_g is related to significant dimensional, structural and/or functional properties and more specifically, to the number of nearest MO_x polyhedral neighbors and the number of bonds between each of those neighbors.^[26] E_{a} values from the optical absorption edges can thus trace the evolution of the structure of supported species as a function of loading. The specific catalytic activity of the supported Ti catalysts was directly correlated to their corresponding E_{α} (inset in Figure 2D). The TOF increases monotonically from 4 to 114 h⁻¹ for 30 wt% ($E_g = 3.33 \text{ eV}$) and 0.4 wt% TiO₂/SiO₂ ($E_g = 4.3 \text{ eV}$) respectively. Although all these TiO₂/SiO₂ catalysts are highly selective to LD (selectivity 88-90%, Figure S23), this relation suggests that the specific catalytic activity of the different surface Ti species decreases in the following order: isolated $TiO_4 >$ polymerized TiO_4 > polymerized TiO_5 > polymerized TiO_6 species. It is currently unclear whether these differences in reactivity are due to the participation of the weaker Ti-O-Si bonds in the reaction (by bond breaking and generation of a vacant Lewis acid site, such as it has been observed for methanol oxidation reactions^[21]), or due to changes in the strength of the (Lewis) acidity such as suggested in the liquid transesterification of refined oil with methanol^[29]. However, similar apparent activation energies (51.7-56.8 kJ mol⁻¹) were calculated for LD production from MLA with three different TiO₂ loadings on SiO₂ (resp. 1, 5 and 20 wt%, Figure S24), which suggests that kinetics are more related to the number of Ti-O-Si bonds through the pre-exponential factor than to the Lewis acidity of the Ti-sites. More mechanistic studies are however required.

In conclusion, a direct catalytic route to LD, the key PLA bioplastic intermediate, has been established based on the gas-phase transesterification of alkyl lactates. TiO_2/SiO_2 catalysts provide an excellent selectivity to LD of up to 90%. The remaining fraction mainly consists of recyclable ML₂A, with negligible amounts of lost side-products and LD racemization. Under optimized conditions, productivities up to 8 g_{LD} g_{cat} h⁻¹ can be attained under continuous operation in a scalable fixed-bed setup. The catalytic performance

of the active TiO₂ phase is modified by interaction with the SiO₂ support through the formation of Ti-O-Si bonds. The specific catalytic activity of the TiO₂ phase was strongly correlated to its electronic and geometric features as derived from DR UV-VIS spectroscopy. TiO₂/SiO₂ catalysts having a higher band gap energy were more active for LD production, indicating that increased number of weak Si-O-Ti bonds and low coordination numbers of the Ti-site are essential for the MLA to LD transesterification conversion on Ti-based catalysts.

Experimental Section

Experimental details and additional information on reaction thermodynamics can be found in the supporting information (SI).

Acknowledgements

R.D.C. thanks IWT (Agency for Innovation by Science and Technology, project number 131404) for financial support. M.D. acknowledges FWO Vlaanderen and BOFZAP. M.D, E.M. and B.F.S. thank the Industrial Research Fund (IOF, grant ZKC8139). Prof. P. Vereecken, X. Chen and T. Nuytten are thanked for their help with Raman spectroscopy measurements.

Keywords: gas phase • lactide • supported catalysts • sustainable chemistry • transesterification • alkyl lactates

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Closing the ring: a new production process is proposed for the synthesis of lactide, a cyclic building block of bioplastics, via the gas-phase transesterification of alkyl lactates. This process substantially simplifies current inefficient synthesis routes. Supported TiO_2/SiO_2 catalysts exhibit high LD selectivity. Their specific catalytic activity is strongly correlated to its band gap energy. Specific catalytic activity strongly increases upon decreasing Tipolymerization.



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