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Oxidation of levulinic acid for the production of maleic anhydride: breathing new life into biochemicals[†]

Anargyros Chatzidimitriou and Jesse Q. Bond*

Levulinic acid (LA) is a biomass-derived platform chemical that could play a central role in emerging industries as an intermediate that facilitates production of bio-based commodities. In this context, we present a novel, catalytic pathway for the synthesis of maleic anhydride (MA) *via* oxidative cleavage of the methyl carbon in LA over supported vanadates. The approach is demonstrated in a continuous flow, packed bed reactor, and we have observed that VO_x supported on SiO₂ achieves single-pass MA yields as high as 71%. Preliminary analysis suggests that LA might compete with butane as an industrial MA feed-stock. Finally, bifunctional LA and monofunctional 2-pentanone display contrasting oxidative cleavage selectivities, indicating that methyl carbon cleavage during vapor phase oxidation over supported vanadates is unique to LA.

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Introduction

Concern over diminishing fossil reserves and the environmental impact of their utilization has expanded interest in the production of bio-based commodities. In this respect, abundant lignocellulose is often viewed as an ideal alternative source of industrial carbon. Because the transportation sector accounts for the bulk of oil consumption, lignocellulosic biofuels are commonly proposed as an avenue for mitigating oil reliance; unfortunately, lignocellulosic carbon is locked in oxygen-rich polysaccharides and lignin. In biofuel production, their inherent functionality is problematic because the ideal target products-liquid alkanes-are devoid of heteroatoms and functional moieties. Although technologically possible, synthesizing energy-dense fuels from lignocellulose requires extensive feedstock defunctionalization, substantial hydrogen input, and (frequently) carbon-carbon bond formation.¹ Accordingly, advanced biofuels are cumbersome and expensive, and they have failed to compete in current markets.

With the caveat that biorefineries must target production of saleable, large-market commodities, lignocellulose is more likely to succeed as a feedstock where its inherent functionality—instead of comprising the central challenge—offers a distinct competitive advantage. In this context, partially

E-mail: jqbond@syr.edu; Tel: +(315)443-2550

oxygenated hydrocarbons are an attractive class of products. Their functionality makes them useful intermediates in numerous applications; thus, they have robust, established markets. Further, from a petroleum chemistry standpoint, they are challenging targets that require oxidative functionalization of relatively inert feedstocks. Typically, this occurs under severe conditions and forms products that are more reactive than their precursors; hence, it is difficult to control selectivity, and oxygenated hydrocarbons are expensive relative to alkane fuels.²⁻⁴ In general, functionally equivalent oxygenates can be produced from biomass through partial deoxygenation, which is frequently attractive compared to alkane functionalization. Because oxygen imparts reactivity, one can often transform biomass under mild conditions, where judicious catalyst selection can control product selectivity. As a chemicals feedstock, biomass thus becomes increasingly attractive relative to fossil hydrocarbons with the amount of oxygen in the target product. With these criteria in mind, we contrast petrochemical production of maleic anhydride (MA) with an alternative approach based on the oxidation of levulinic acid (LA).

MA is a petrochemical commodity that has a relatively high oxygen content (O : C = 0.75), and it is challenging to manufacture *selectively* from hydrocarbons. Further, it is used industrially for the production of butanediol, tetrahydrofuran, γ -butyrolactone, 2-pyrrolidone, *N*-methyl-2-pyrrolidone, and a range of polymers and surfactants such that it has a well-established market.^{5,6} MA can be supplied through the aerobic oxidation of butane (0.30–0.70 \$ per kg, 2014) or benzene (0.80–1.60 \$ per kg, 2014).^{5,7,8} Benzene oxidation occurs over supported vanadium oxides at temperatures from 623–673 K.

Department of Biomedical and Chemical Engineering, College of Engineering & Computer Science, Syracuse University, Syracuse, NY 13244, USA.

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It is generally the more selective route, delivering single pass MA yields in excess of 70%. Alternatively, vanadium-phosphorous oxides (VPO) are used to produce MA through butane oxidation at slightly higher temperatures (663-703 K). Under industrial conditions, optimal MA selectivities (65-75%) are reported at roughly 85% butane conversion, giving maximum single pass yields of 50-60% during butane oxidation. Although benzene oxidation is milder and slightly more selective, it is not sufficiently so in either respect to offset the cost of using benzene as an MA feedstock, and butane oxidation has become the dominant technology.9 Over the last decade, MA prices have ranged from 1.50-2.00 \$ per kg in a global market of roughly 1500-2000 kilotons per annum (kta).^{10,11} Presently, MA prices are on the lower side of this range, which likely stems from the recent expansion of oil and natural gas production in the United States.⁷ Based on butane prices over the past year and reported MA yields of 70% under industrial conditions of full recycle, we estimate that butane purchasing will contribute \$0.25-\$0.60 per kg to the cost of MA production.

As an alternative, we have found that levulinic acid (LA) can be employed as an MA precursor. LA is a 5-carbon keto-acid that can be synthesized from hexose- and pentose-containing polysaccharides that comprise the bulk of lignocellulose (Fig. 1).

Pathways for LA production from both C5 and C6 sugars are well-described, and the underlying methodologies extend to numerous biomass feedstocks.¹²⁻¹⁴ LA itself has no substantial commercial demand; however, it offers intriguing chemical functionality and can be upgraded to multiple *potentially* saleable products including oxygenated fuel additives such as gamma-valerolactone,^{15–21} methyltetrahydrofuran,^{22,23} alkyl levulinates,24,25 and alkyl valerates;26 alkane fuels;27-32 and niche specialty chemicals, such as the herbicide δ -aminolevulinic acid (DALA).33 First generation attempts at commercialization of LA-based refineries have largely explored production of biofuels, such as ethyl levulinate; however, due to the aforementioned challenges facing the production of lignocellulosic biofuels, LA has made little headway in the transportation sector, and development of LA-based refineries remains stagnant. We were thus intrigued to learn that simple, vaporphase, aerobic oxidation of LA over supported vanadates delivers MA at 71% of the theoretical maximum yield. Good MA



Fig. 1 Bio-based and petrochemical strategies for the production of maleic anhydride (MA).

selectivity is attainable at temperatures of 573-598 K, which is mild compared to conventional butane oxidation (663-703 K). Further, MA has an established market and is (on a molar basis) roughly ten-fold more valuable than refinery alkanes, suggesting that it could be an attractive commercial target for emerging LA producers. Before discussing the approach further, we note that two prior reports have outlined MA production via liquid-phase oxidation of 5-hydroxymethylfurfural (HMF) over VO(acac)₂ (53% MA yield)³⁴ and vanadium substituted heteropolyacids (64% MA yield).35 Because HMF produces LA upon hydrolysis, these approaches might entail similar chemistries to those described here; however, LA is favored as an MA feedstock from a practical standpoint. HMF is difficult to prepare selectively from lignocellulose since it generally requires either a preliminary glucose-fructose isomerization step or the use of exotic systems,^{36,37} whereas LA can be prepared directly from cellulose via dilute acid hydrolysis.33 This suggests that LA will always be a lower cost commodity than HMF and thus a more realistic MA precursor.

From an economic standpoint, BioFine has indicated that cellulose-derived LA can be produced for roughly \$0.21 per kg.³³ Based on this price and a yield of 70%, the cost of LA would contribute roughly \$0.36 per kg to MA manufacture, which is comparable to estimated butane expenses in the conventional approach. While BioFine's figure is likely optimistic, LA production costs could increase roughly 2.5-fold to \$0.53 per kg before LA is unable to compete with butane at \$1.05 per kg, where it peaked in 2008 and approached in 2012.⁷ Certainly, the LA-based approach becomes more attractive as the price of butane increases. Further, although 70% is likely a ceiling on attainable MA yields during well-optimized butane oxidation under recycle conditions, we see no reason that the best single-pass yield reported here (71%) represents an upper limit on attainable MA selectivity during LA oxidation; therefore, future optimization could make the LA-based approach even more attractive.

Our preliminary assessment of process economics is simplistic, relying solely on a comparison of estimated feedstock costs for the carbon source in butane- and LA-based strategies for MA production. Although it is essential that detailed design studies consider additional aspects of these processes, including reactor sizing; materials of construction; operating temperatures and pressures; separations; and feed recycle before concluding that an LA-based strategy could be profitable in the near term, initial feasibility determinations are generally best made by assessing the economic potential of a technology based on raw material costs and revenue generated through product sales.³⁸ For the purposes of demonstrating that an LA-based approach could potentially be feasible alongside present inexpensive butane, the above analysis is sufficient.

Results and discussion

Prior to summarizing trends in LA conversion and product selectivity with variation in operating conditions and catalyst

selection, we facilitate a comprehensive discussion of selectivity by considering the landscape of oxidative and non-oxidative reactions that occur in this system.

As shown in Fig. 2, the primary reaction leading to MA is likely oxidative cleavage of the C₄-C₅ bond of LA. According to mechanistic insights gleaned from 2-butene and 2-butanone oxidation, this cleavage should result in formation of equimolar quantities of succinic acid and formaldehyde.^{39,40} We note that the formation of succinic acid and formaldehyde from LA occurs with $\Delta G \approx -326$ kJ mol⁻¹ at 548 K, and we thus expect oxidative cleavage to occur irreversibly. Succinic acid can then reversibly form its anhydride by dehydration, which is thermodynamically favorable over the temperature range considered here ($\Delta G \approx -11.6$ kJ mol⁻¹ at 548 K). Because of the relatively high temperatures and low water partial pressures in our system, succinic anhydride (SA) should be the dominant (equilibrium) form of succinic acid at our experimental conditions. Selective formation of succinic acid/ succinic anhydride (70-80% vield) via vapor-phase oxidative cleavage of LA has been reported by Dunlop in the patent literature,⁴¹ but this result has not been confirmed in the peerreviewed literature. Our experiments have employed similar catalysts and conditions to those described in Dunlop's patent; however, MA was instead recovered as the dominant oxidative cleavage product whereas SA was only observed in

trace quantities (<1%). This suggests that, in line with mechanistic expectations, SA forms as the initial cleavage product but subsequently undergoes oxidative dehydrogenation (ODH) to form MA. ODH is kinetically possible over supported vanadates,^{42,43} and it is thermodynamically favorable under our reaction conditions. For reference, the oxidative dehydrogenation of succinic anhydride to form maleic anhydride occurs with $\Delta G \approx -157$ kJ mol⁻¹ at 548 K. MA should thus form irreversibly and be the dominant product so long as LA oxidative cleavage is slow relative to SA oxidative dehydrogenation (otherwise, SA would be observed as a major product based on the proposed reaction pathways). The anticipated C₁ coproduct, formaldehyde, was never observed in our experiments; however, it is reasonable to expect that formaldehyde will further oxidize to formic acid and/or carbon oxides (CO_x) under the reported conditions. Here, CO_x were the only experimentally observed C1 products, implying that the coproduct of MA formation is always lost to combustion.

Just as cleavage of the C_4 - C_5 bond of LA leads to C_1 and C_4 products, analogous cleavage of the C_3 - C_4 bond should result in C_2 (acetaldehyde or acetic acid) and C_3 products (3-oxopropanoic acid or malonic acid). Both acetaldehyde and acetic acid were detected; however, their formation cannot be solely attributed to C_3 - C_4 bond cleavage since sequential cleavage of C_4 products may also form C_2 products. Malonic acid and



Fig. 2 Pathways consuming LA and its derivatives during oxidation over supported vanadates.

3-oxo-propanoic acid were never observed, but this cannot be taken as conclusive evidence that C_3 - C_4 cleavage does not occur. Malonic acid is thermally unstable and will decarboxylate to form CO_2 and acetic acid at 343 K;⁴⁴ therefore, it is unlikely to be recovered under our conditions. Acrylic acid and propionaldehyde were observed in trace quantities (<0.5% selectivity). These species likely form through non-oxidative C-C scission (*i.e.*, cracking) of levulinic acid and/or reaction intermediates.

At high temperatures and in the presence of acid sites, LA dehydration leads to the formation of α -angelical actone (AAL, $\Delta G \approx -11$ kJ mol⁻¹ at 548 K) and β -angelical actone (BAL, $\Delta G \approx$ -10 kJ mol⁻¹ at 548 K).⁴⁵ Methylvinylketone (MVK) also forms alongside CO through decarbonylation of LA.46 Reaction products additionally contained C5 diones (DIO), specifically 1,3cyclopentanedione (DIOS) and its dehydrogenated analog, 4-cyclopentene-1,3-dione (DIOU). DIOS is an isomer of α and β-angelicalactone, and electronic structure calculations suggest that its formation from either angelicalactone (ANG) is slightly favorable, occurring with $\Delta G \approx -1$ to -2 kJ mol⁻¹ at 548 K. DIOS is thus anticipated in appreciable quantities over this range of temperatures, provided that its formation is not limited by the rate of ANG isomerization. Subsequently, ODH of DIOS should result in irreversible formation of its unsaturated analog, DIOU ($\Delta G \approx -177$ kJ mol⁻¹ at 548 K). Our observation that DIOU is generally the dominant DIO form reinforces our conclusion that oxidative dehydrogenation is facile under our experimental conditions. It is worth mentioning that DIOS and DIOU are both intriguing, multifunctional molecules. To our knowledge, their synthesis from LA has not been previously reported, and future efforts directed toward optimizing their selectivity may establish them as a new class of bio-based platform intermediates. Finally, over the reported temperature range, any C_n species illustrated in Fig. 2 might additionally undergo complete or partial combustion, resulting in the formation of nCO_x . In each experiment described below, all detectable reaction products were quantified, and carbon balances closed to within 12%.

 γ -Al₂O₃ has a relatively high surface area, it supports good vanadate dispersion at high areal loadings, and the patent literature indicates it as a preferred vanadate support for the oxidative cleavage of LA.⁴¹ Accordingly, our initial investigations probed the influence of operating conditions on LA conversion and product selectivity over VO_x/ γ -Al₂O₃ (Fig. 3).

LA conversion increases with temperature and contact time until 598 K, where complete LA conversion is observed at all contact times. MA selectivity is favored by increasing reaction temperature, which suggests that oxidative cleavage of LA proceeds with a higher barrier than competing side reactions. At all temperatures, we further observe that MA selectivity improves with contact time even under conditions of complete LA conversion (see 598 K, Fig. 3). This may indicate that MA forms as a secondary product during LA oxidation. Over VO_x/ γ -Al₂O₃, the highest MA selectivities (50–60%) were observed under conditions of complete LA conversion at 598 K and contact times from 4-16 min. Because of the complexity of this reaction landscape, it is difficult to assign molar selectivities to all products as we have done for MA. Accordingly, Fig. 4 summarizes complete carbon distributions for the reaction products recovered during LA oxidation over VO_x/γ -Al₂O₃.

Only ANG, MA, DIOU, and CO_x were produced in substantial quantities (>5%), and their percentages are given discretely in Fig. 4. Note that both AAL and BAL are included in the ANG label. Acetic acid, acrylic acid, acetaldehyde, propionaldehyde and MVK were observed in sufficient quantities to warrant inclusion in the carbon balance (1–5%), and these species are lumped into the category "other."

Below 573 K, angelicalactones dominate the product distribution. Their selectivity decreases slightly with increasing



Fig. 3 LA conversion and MA selectivity as a function of temperature and contact time over VO_x/γ -Al₂O₃. MA selectivity is defined as the molar quantity of MA formed normalized by the molar quantity of LA consumed. Contact times are calculated as the molar loading of vanadium in the reactor normalized by the molar feed rate of LA. $p_{LA} = 0.016$ bar, $p_{O_y} = 0.33$ bar.

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Fig. 4 Product carbon distributions as a function of contact time. (a) 523 K, (b) 548 K, (c) 573 K, (d) 598 K.

contact time and dramatically with increasing temperature. At 573 and 598 K, product selectivity shifts primarily toward MA and CO_x, and they displace ANG as the major reaction products. This is tentatively attributed to LA dehydration being (apparently) kinetically facile relative to oxidative cleavage. At low temperatures, the extent of LA oxidation is insignificant, and the bulk of LA consumption occurs through dehydration to form ANG. If oxidative cleavage is a higher barrier process than dehydration, it is plausible that temperature increases shift selectivity toward oxidative cleavage products. Further, LA dehydration is endothermic and, while it becomes thermodynamically favorable, it is not irreversible in this temperature range ($\Delta G \approx -7$ to -18 kJ mol⁻¹ from 523–598 K); therefore, ANG yields are likely equilibrium limited, and ANG should revert to LA if the equilibrium position is displaced by LA consumption. Elevated temperatures increase the rate of irreversible oxidative cleavage of LA and should therefore drive the system to complete conversion and shift selectivity toward MA and CO_x . Alternatively, it may be possible that direct oxidative cleavage of either ANG or DIOS leads to MA formation. This is potentially consistent with increasing MA selectivities as a function of contact time; however, the mechanism of such is presently uncertain.

Thermodynamic analysis of the landscape shown in Fig. 2 reveals further insights into phenomena governing selectivity in this system. Oxidative cleavage of LA to produce SA and ODH of SA to form MA are both exceedingly favorable and should be considered irreversible. In contrast, with the exception of oxidative dehydrogenation of DIOS, each step leading to the formation of DIOU should occur favorably, but reversibly. We therefore expect that, given a sufficient residence time, LA, AAL, BAL, and DIOS can all ultimately be converted to either MA or DIOU. Both of these form irreversibly; thus, the distribution of MA and DIOU in the reaction products is likely controlled by the relative rates of two key (irreversible) reactions: oxidative cleavage of LA and oxidative dehydrogenation of DIOS. Increasing reaction temperature appears to shift selectivity toward MA at the expense of DIOU, suggesting that oxidative cleavage of LA proceeds with a higher barrier than oxidative dehydrogenation of DIOS. Finally, we observe that increases in MA selectivity are always accompanied by an increase in CO_x selectivity. We expect that the C_1 coproduct of LA oxidative cleavage should form CO_x under our conditions; thus, a commensurate increase in CO_x yield with MA yield is anticipated. However, stoichiometry implies that LA oxidative cleavage should result in product carbon distributed between

 CO_x and MA in a 1:4 ratio, whereas we generally observe ratios on the order of 1:1. This suggests that multiple pathways lead to CO_x in this system.

The influence of molecular oxygen was considered over VO_x/γ -Al₂O₃, and our observations are presented in Fig. 5.

Even under oxygen lean conditions (0.010 bar O_2 , O_2 : LA = 0.62), we observe baseline conversion of LA. This is attributed to non-oxidative pathways, primarily dehydration, such that ANG comprised 80% of the product carbon distribution. An additional 16% of the product carbon existed as DIO, with DIOS and DIOU recovered in 5:3 molar ratio. It is worth noting that increasing O₂ pressure shifts the DIO distribution completely toward the unsaturated product, DIOU, which is consistent with our interpretation that DIOU forms via ODH of DIOS. LA conversion increases with O₂ partial pressure (Fig. 5b), and we attribute this to an increase in the rates of irreversible, oxidative reactions that allow complete consumption of LA, ANG, and DIOS and shift selectivity toward DIOU, MA, and CO_x. Increasing O₂ pressure initially favors DIOU formation, while further increments drive formation of MA and CO_x. Fig. 5b illustrates a clear, first order dependence of MA selectivity on O₂ pressure. Since SA, MA, and DIOU all form irreversibly, this enhancement in MA selectivity is likely attributed to a disproportionate increase in the rate of LA oxidative cleavage relative to the rate of DIOS dehydrogenation in response to increases in O_2 pressure, *i.e.*, irreversible oxidative cleavage of LA appears higher order in O_2 than does irreversible ODH of DIOS.

Because the majority of steps outlined in Fig. 2 are proposed to be reversible, efforts to enhance the selectivity of MA in this system can be reduced to two goals: suppressing irreversible formation of DIOU via ODH and controlling irreversible formation of CO_x . Both might plausibly be addressed by varying the nature of the catalyst support. Bifunctional LA is sensitive to the acid/base character of the catalyst, and such functionalities could reduce MA selectivity. For example, ANG formation is promoted by acid sites; as such, an acidic support could facilitate DIOS formation and thus drive selectivity toward DIOU. Further, the oxidative capacity of supported vanadates generally increases with the reducibility of the support.47 Accordingly, decreasing support reducibility may help to limit the extent of over-oxidation in this system. Support influence was examined by comparing the performance of VOx/y-Al2O3 to that of VOx/SiO2, VOx/TiO2, and unsupported V₂O₅. Results are summarized in Table 1.



Fig. 5 Influence of O₂ partial pressure on LA conversion and MA selectivity. T = 623 K, $p_{LA} = 0.0158$ bar, WHSV = 0.128 min⁻¹.

| Table 1 | Comparison of IA | avidation avan | bull and aun | norted venedat | | aludaa bath l | |
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| Table T | Companson of LA | Oxidation over | buck and sup | porteu variauat | es. DIO III | cludes both | DIOS and DIOU |

| Entry | Catalyst | <i>T</i> (K) | τ^{a} (min) | Conversion (%) | MA yield (%) | Carbon distribution (%) | | | | | (The second seco | |
|-------|-----------------------------------|--------------|------------------|-------------------|-----------------|-------------------------|----|--------|-----|-------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| | | | | | | ANG | MA | CO_x | DIO | Other | $MA: CO_x$ | (%) |
| 1 | VO _x /SiO ₂ | 548 | 1.95 | 99 | 50 | 2 | 43 | 36 | 15 | 4 | 1.2 | 96 |
| 2 | VO_x/TiO_2 | 548 | 0.39 | 93 | 26 | 3 | 25 | 61 | 8 | 3 | 0.4 | 89 |
| 3 | VO_x/Al_2O_3 | 548 | 78 | 98 | 33 | 5 | 27 | 34 | 26 | 8 | 0.8 | 100 |
| 4 | V_2O_5 | 548 | 280 | 97 | 18 | 12 | 15 | 21 | 45 | 7 | 0.7 | 98 |
| 5 | VO_x/SiO_2 | 523 | 3.9 | 43 | 1 | 83 | 2 | 5 | 8 | 2 | 0.5 | 98 |
| 6 | VO_x/SiO_2 | 548 | 3.9 | 100 | 48 | 1 | 44 | 35 | 14 | 6 | 1.3 | 88 |
| 7 | VO_x/SiO_2 | 573 | 3.9 | 100 | 71 | 0 | 57 | 37 | 2 | 4 | 1.5 | 100 |

^a Contact time. ^b Carbon balance.

At 548 K, VO_x/SiO_2 and VO_x/TiO_2 are significantly more active than VO_x/γ -Al₂O₃ and V_2O_5 (entries 1–4). Both achieve complete LA conversion at contact times below 2 min, whereas complete LA conversions were not achieved until contact times of roughly 80 min over VOx/7-Al2O3 and 300 min over bulk V₂O₅. Comparing selectivities at complete LA conversion, we observe that MA selectivity increases with catalyst identity in the order of $V_2O_5 < VO_x/TiO_2 < VO_x/\gamma - Al_2O_3 < VO_x/SiO_2$. Each material showed comparable selectivities toward ANG (<15%), while the remaining product distribution varied with support identity. Bulk V₂O₅ appears relatively selective toward DIOU, which comprises 45% of the product carbon distribution. This suggests that bulk V₂O₅ facilitates DIOS dehydrogenation to a greater extent than it does LA cleavage. DIOU selectivity decreases over VO_x/γ -Al₂O₃ (26%) and further over VO_x/SiO_2 (15%) and VO_x/TiO₂ (8%). Over bulk V₂O₅, VO_x/ γ -Al₂O₃, and VO_x/TiO_2 , carbon selectivity towards CO_x exceeds that of MA, suggesting these materials promote combustion more so than oxidative cleavage. Only VO_x/SiO_2 achieves an MA: CO_x carbon ratio greater than unity, implying that it is effective at limiting over-oxidation. Since VO_x/SiO₂ appeared to suppress both DIO and CO_x formation, it was further examined (entries 5–7). Consistent with results obtained over VO_x/γ -Al₂O₃, MA selectivity increases dramatically with temperature over VO_x/SiO₂. At 573 K, we obtained an MA (carbon) selectivity of 57% and a MA: CO_x ratio of 1.54, which corresponds to a molar MA yield of 71%. It is evident that the nature of the support can impact activity and selectivity in this system; however, each support employed here varies in its acid/base character, and the structure and function of VO_x clusters varies strongly with support and VO_x loading.⁴⁸ Probing fundamental sources of the observed variations will require a more comprehensive characterization study than is warranted in the present discussion.

It is interesting to note that insights from the 2-butanone oxidation literature suggest that MA is an unanticipated product in this system.^{40,49,50} Oxidative ketone cleavage is mediated by enol formation, and enolization of any methyl ketone—a designation that includes both LA and 2-butanone —should lead to one of two possible enol forms. One will have a C=C bond in the terminal position, and one will have a C=C bond in an internal position (Fig. 6).

In the case of 2-butanone, the internal enol is more stable, 50,51 and its oxidative scission yields two C_2 products,



Fig. 6 Enol mediated oxidative cleavage of methyl ketones.

acetaldehyde and acetic acid, whereas analogous cleavage of the terminal enol will form formaldehyde (C_1) and propanoic acid (C_3). Prior studies of 2-butanone oxidation have reported overwhelming selectivity toward C_2 products rather than C_1/C_3 products,^{40,49,50} suggesting that product selectivity reflects enol stability. Electronic structure calculations indicate that the internal enol of LA is also the more stable form such that one might similarly expect internal C–C cleavage during LA oxidation.

Oxidative cleavage of LA's methyl group (to form SA) has been previously reported;^{52–55} however, most accounts describe condensed-phase oxidations and/or homogeneous oxidants, and there is evidence that these systems will induce terminal C–C cleavage in *any* methyl ketone.⁵² In contrast, the only description of selective cleavage of the terminal carbon during gas-phase oxidation of methyl ketones was reported in Dunlop's patent, which describes LA oxidation over supported vanadates.⁴¹ His observations and those reported here suggest that the unique selectivity in this system arises from the bifunctional nature of LA. To probe this, we compared the oxidative cleavage of LA to its nearest monofunctional ketone analogue, 2-pentanone (Table 2), and we observed comparable oxidative cleavage rates with each molecule.

Consistent with prior accounts of 2-butanone oxidation, 2-pentanone oxidation primarily yields internal scission products (C_2 and C_3 aldehydes/acids) whereas only trace quantities of C_4 products were recovered. In contrast, roughly 80% of the cleavage selectivity during LA oxidation goes to C_4 cleavage products, namely MA. This implies a unique stabilization of terminal C–C cleavage during LA oxidation; however, we

| Table 2 | Comparison of oxidative cleavage rates and C ₄ selectivities for LA and 2-pentanone on VO_x/γ -Al ₂ O ₃ | | | | | | | | | |
|---------|-------------------------------------------------------------------------------------------------------------------------------------------------|-----------------|----------------------------------------|---------------|-------------------|------------------------------------------------------------|---------------------------------------------------------|------------------------|--|--|
| Entry | Feed | $T(\mathbf{K})$ | Feed rate (µmol min ^{−1}) | $	au^a$ (min) | Conversion (%) | Cleavage rate (µmol min ⁻¹ g ⁻¹) | $\begin{array}{c} \mathbf{C_4}^{b} \\ (\%) \end{array}$ | CB ^c (%) | | |
| 1 | 2-Pentanone | 573 | 79 | 7.80 | 14 | 22 | 1 | 96 | | |
| 2 | 2-Pentanone | 585 | 79 | 7.80 | 49 | 35 | 2 | 96 | | |
| 3 | 2-Pentanone | 598 | 79 | 7.80 | 95 | 59 | 3 | 96 | | |
| 4 | LA | 573 | 79 | 7.80 | 99 | 41 | 85 | 90 | | |
| 5 | LA | 598 | 79 | 7.80 | 100 | 50 | 89 | 90 | | |

^{*a*} Contact time. ^{*b*} Ratio of product carbon recovered in C_1 and C_4 (terminal) cleavage products to the total quantity of carbon recovered in oxidative cleavage products. ^{*c*} Carbon balance.

cannot pinpoint the mechanism by which this occurs without further characterization of catalytic sites and oxidation kinetics.

Materials and methods

Reagents

Bulk vanadium pentoxide (98%, Acros) was used with no further preparation. γ -alumina (low soda, Strem Chemicals), titanium oxide (Aeroxide® P25, Acros), amorphous silica (99% Davisil grade 633, Sigma), ammonium metavanadate (99% Sigma) and oxalic acid (98% anhydrous, Acros) were used for catalyst synthesis. Maleic acid (98%, Fisher), acetaldehyde (99.5%, Sigma), acetic acid (99.8%, Acros), propionaldehyde (99%, Acros), propionic acid (99%, Acros), acrylic acid (99%, Acros), 4-cyclopentene-1,3-dione (95%, Sigma Aldrich), butenone (99%, Sigma), α-angelica lactone (MP Biomedicals), CO (99.99% Praxair) and CO₂ (5% in N₂, Airgas) were used as supplied from the manufacturers for standard preparations and instrument calibrations. Acetone (99.9%, Fischer) was used as a solvent for all reactor samples and standard preparations. Levulinic acid (LA, 98%, Sigma Aldrich) and 2-pentanone (99%, Acros) were used as reactor feeds. Purified water used in catalyst preparation and HPLC mobile phases was prepared in house by sequential reverse osmosis, UV oxidation, and double ion exchange. He (99.999%, Airgas) was used as a diluent, O2 (99.999%, Airgas) and O_2 (1% in He with 1% Ar, Praxair) were used as oxidants, while air (Zero and Medical Grade, Airgas) was used for calcinations both in the catalyst synthesis phase and for the in situ calcination of the catalytic reactor prior to reaction.

Catalyst synthesis

 γ -Al₂O₃, TiO₂ and amorphous SiO₂ were considered for catalyst synthesis. Catalysts were prepared by evaporation to dryness of a mixture consisting of the support and ammonium metavanadate dissolved in aqueous, 1 M oxalic acid. The molar quantity of vanadium employed for each support was calculated based on the BET surface areas of the oxide supports (Table 3), obtained using a commercial system (Micromeritics ASAP 2020), with the aim of creating an amorphous, two-dimensional vanadia monolayer in contact with the oxide support.

For Al_2O_3 and TiO_2 supports, $9.5VO_x/nm^2$ was the targeted coverage, while in the case of the SiO₂ support, the coverage

was limited to $2.7 \text{VO}_x/\text{nm}^2$, due to the low density and reactivity of the surface hydroxyls.⁵⁶ The vanadate solution was added to the support and the resulting slurry was evaporated at 338 K under continuous mixing. The catalyst was crushed and sieved to achieve uniform particle size and finally was activated by holding the sample under flowing air for 4 hours at 773 K.

Reactor setup

All reaction experiments were run in the gas phase in a 1/2" downflow stainless steel tubular reactor. The catalyst bed was held halfway through the length of the tube between two pieces of quartz wool, while the remainder of the tube was filled with quartz chips to ensure uniform mixing and minimize the dead volume of the reactor. A 12" long ceramic furnace (Omega) was used to heat the reactor. Prior to each experiment, the catalytic reactor was calcined at 773 K for 4 hours.

A preheated mixing section was held at a temperature of 423 K, and separate feeds of LA (introduced using a syringe pump, Cole Parmer Series 100) and a gas stream consisting of O_2 and He (controlled by mass flow controllers, Valco model 100), were first heated to 423 K and introduced to the mixing stage. The flowrates of LA, O_2 , and He were adjusted to achieve the desired LA and O_2 partial pressures. The entire delivery system was heat traced, and LA partial pressures were always held below LA vapor pressure at the system temperature to prevent condensation. The gaseous mixture was subsequently heated to reaction temperature in a preheating stage and then introduced into the reactor. All temperatures were monitored with K-type thermocouples (Omega) and controlled using PID controllers (Series 16A, Love Controls).

At the exit of the catalytic reactor, the gaseous effluent was scrubbed using an acetone filled trap, which was typically immersed in an ice bath to allow rapid cooling and capture of condensable reaction products. After initial introduction of LA and oxidant feeds to the catalyst bed, reactors were permitted 48 hours to reach a steady state. Data reported here were subsequently collected over roughly 200 hours on stream for a given catalyst sample. During this time, reactors were periodically returned to the initial operating conditions, and comparison of rates to the initial steady state data indicated that no significant activity losses occurred over the course of a given experiment. Though long-term stability was not assessed, catalysts employed here were observed to be fully regenerable for multiple reaction cycles (\approx 5) *via* calcination in air at 773 K.

| Table 3 | Surface area characterization of employed catalysts | | | | | | | | |
|---------|-----------------------------------------------------|------------------|------------------|-----------------------------------------------------------|----------------------------------------------------------------|--------------------------------------|--|--|--|
| Entry | Catalyst | Support | Weight % of V | Support S_{BET} $(\text{m}^2 \text{ g}^{-1})$ | Catalyst S_{BET} (m ² g ⁻¹) | Surface density (V atoms per nm²) | | | |
| 1 | V_2O_5 | n/a | 56 | n/a | 4 | | | | |
| 2 | VO_x/γ -Al ₂ O ₃ | Al_2O_3 | 15.7 | 231 | 216 | 9.5 | | | |
| 3 | VO_x/SiO_2 | SiO ₂ | 9.6 | 481 | 333 | 2.6 | | | |
| 4 | VO_x/TiO_2 | P25 | 4.3 | 56 | 31 | 9.5 | | | |

All product species reported here, with the exception of CO_r were recovered in the condenser. All condensed species, with the exception of MA, were quantitatively analyzed by an Agilent 7890 GC equipped with an FID detector and an HP-INNOWAX column. MA was quantified using an Agilent series 1100 HPLC equipped with a Hi-Plex column. For this analysis, we employed a pH 2 aqueous H₂SO₄ mobile phase and quantified MA concentrations using a VWD detector. Because of the relatively high temperatures and low water partial pressures in our reactor, we anticipate that MA exits our reactor as its anhydride; however, because of the aqueous nature of our analysis, MA was quantified here as maleic acid. The vapor phase (CO_r) was sent to an in-line chromatograph (GC 7890 Agilent). CO₂ was resolved from CO using a packed column (Restek Shin-Carbon ST Micropacked) and quantified via TCD response relative to a helium reference.

Qualitative product identification was achieved using an Agilent 7890 GC-MS equipped with an Agilent 5975C MS detector and an HP-INNOWAX column. Diacid and anhydride peaks were poorly resolved in the HP-INNOWAX column. To make qualitative product assignments and confirm the presence of C_4 diacids and anhydrides in our reaction products, the product stream was bubbled through methanol. This converted diacids (succinic, maleic, and fumaric) and their anhydrides into their methyl and dimethyl esters, which were easily resolved *via* GC-MS and could be identified from their fragmentation patterns (ESI[†]).

Conclusion

In summary, we have demonstrated that MA can be produced in good yield and continuous operation (71%) *via* aerobic, oxidative cleavage of LA over vanadium oxides. This route is facilitated through a mechanism that is unique for bifunctional LA and offers an exciting link between lignocellulosic biomass and large, existing commodity markets. Moreover, the inherent reactivity of LA may allow the design of a milder, more selective oxidation strategy, providing it with a competitive advantage over butane as an MA feedstock. In contrast to prior efforts geared toward biofuel production, this approach could offer near-term viability and expand the industrial utilization of lignocellulosic carbon.

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