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Introduction

The 21st century is an exciting time for organic chemists. In the coming decade, we can expect major changes in the production and consumption habits of our society where carbon sources are concerned.¹ The most significant is the advent of electric vehicles running on batteries, which will affect the petrochemicals market.^{2,3} But just as important is the move towards biomass-based bulk- and fine-chemicals.⁴⁻⁶

Biomass can replace fossil carbon sources, primarily through a set of simple building blocks, so-called platform molecules.^{7,8} A good example of these are lactic acid and lactates, which are readily obtained from biomass fermentation.^{9,10} Their market size is already substantial, over \$1.7 billion in 2015.¹¹ They can be converted to important industrial chemicals, including pyruvic acid, acrylic acid, and propanediol.¹² Pyruvic acid and its esters, for example, are used in the food, cosmetics, and agrochemical sectors.^{13,14} The direct catalytic oxidation of lactic acid is a promising route to pyruvic

Designing effective solid catalysts for biomass conversion: aerobic oxidation of ethyl lactate to ethyl pyruvate†

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The direct oxidative dehydrogenation of lactates with molecular oxygen is a promising route for producing bio-based pyruvates. But practical implementation of this route means high yields and mild conditions, which in turn require expensive noble-metal catalysts. Here we report a novel catalytic approach for efficient conversion of ethyl lactate to ethyl pyruvate. We show that vanadia supported on activated carbon acts synergistically with homogeneous pyridine-type additives, giving high conversion and selectivity. Control experiments and simulations show that the reaction follows a two-step pathway: first, the pyridine–lactate complex forms, followed by transfer to the vanadium active site where the oxidation occurs. Building on these results, we design a new solid catalyst where the vanadia sites are impregnated on a pyridine-rich carbonaceous support made from poly(4-vinylpyridine). This catalyst, made from abundant elements, combines the advantages of the homogeneous pyridine additive and the vanadia active site. This combination lowers the local mass-transfer barriers and improves the stability. The catalyst gives over 90% selectivity at 80% conversion at 130 °C and 1 atm oxygen, and can be reused at least five times without losing activity.

> acid, bypassing the current energy-intensive pyrolysis of tartaric acid.^{15,16} But this oxidation is a challenging process, not least because competing over-oxidation pathways lower the product selectivity and yields.

> Several groups have studied this reaction.^{17,18} In the vapour phase, various solid catalysts were reported, including metal oxides and iron phosphates.^{19–21} While these routes show high activity, they are also energy intensive.²² The pyruvate product is easily over-oxidised, lowering the selectivity.²³ This over-oxidation can be suppressed in liquid-phase systems,¹⁴ but the milder conditions typically require noble metal catalysts for oxygen activation.²⁴ Hayashi et al. reported Pd-metal catalysts on activated carbon for the oxidation of lactate to pyruvate in the presence of NaOH.^{25,26} Ding and co-workers used the 3Pb-1Pt/carbon black catalyst for the synthesis of pyruvic acid in good yields, using an excess of LiOH to adjust the pH value.²⁷ Previously, we showed that activated carbon can enhance the product selectivity, inhibiting the pyruvate polymerization in the liquid phase.²⁸ Despite these achievements, however, no simple and cost-effective catalytic system for the oxidation of lactates to pyruvates with oxygen under mild conditions has been reported. Developing such catalysts is essential if we are to really replace fossil-based carbon sources with bio-based ones.

> Here we report that combining vanadium oxide catalysts and base additives creates a catalytic system that can oxidise

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ethyl lactate to ethyl pyruvate with molecular oxygen in high yields. Following on our recent work on mesoporous vanadiatitania catalysts,²⁹ we screened different metal oxides supported on activated carbon, examining the role of basic additives in this oxidation reaction. By combining experiments and simulations, we find that in the presence of pyridine additives, the reaction follows a two-step pathway: the lactate first complexes with the additive and then travels to the vanadium active site. Based on these findings, we design an effective catalyst for this reaction, comprised of a pyridine-rich carbon support impregnated with vanadia sites.

Results and discussion

We started by testing various carbon-supported catalysts for the oxidative dehydrogenation of ethyl lactate to ethyl pyruvate under 1 atm oxygen pressure (eqn (1)). Initially, we tested metal oxides known as good oxidation catalysts for alcohols:^{24,30} iron oxide, cobalt oxide, copper oxide and vanadium oxide, (denoted as MO_x/C). These were compared to commercial Pt/C and Ru/C catalysts. Table 1 summarises the conversion, selectivity, yield and turnover number (TON) values. Fe, Co, Cu and Pt did not catalyse this reaction. Ru/C gave the highest selectivity at 99%, but with a low conversion of 9%. Since VO_x/C showed the highest activity (34% conversion and TON = 223), we decided to focus on the vanadium-based catalyst and try to improve the selectivity through catalyst optimization.

Previous studies by our group and others showed that doping carbon materials with nitrogen atoms can facilitate catalytic oxidation reactions.^{30–32} A key role in this surface activation is probably attributed to pyridinic and pyrrolic nitrogen groups.^{33–36} We therefore decided to study the effects of various nitrogen-containing additives in our reaction system,

 Table 1
 Catalytic oxidation of ethyl lactate with molecular oxygen over various catalysts^a

	OH O ethyl lactate	+ 1/2 O ₂ MO _x /C 130°C, 4h	ethyl pyruvate	+ H ₂ O	(eq 1)
Entry	Catalysts	Conversion ^b (%)	Selectivity ^b (%)	Yield (%)	TON ^c
1	С	Trace	_	_	_
2	CoO_x/C	1	64	0.7	5
3	CuO_x/C	2.2	20	0.4	3
4	FeO_x/C	2.4	47	1.2	8
5	Ru/C^d	9	99	8.9	36
6	Pt/C^{e}	4	97	3.6	140
7	VO_x/C	34	84	29	223

^{*a*} Reaction conditions: Ethyl lactate 5 mmol, 25 mg MO_x/C catalyst (metal loading 0.3 mmol g⁻¹), 1 atm O_2 , diethyl succinate (solvent, 1 ml), 130 °C, and 4 h. ^{*b*} Determined by GC using biphenyl as an internal standard. ^{*c*} Calculated as moles of ethyl pyruvate per moles of metal loading. ^{*d*} Commercial 5 wt% ruthenium on carbon (Ru loading of 0.5 mmol g⁻¹). ^{*e*} Commercial 1 wt% platinum on carbon (Pt loading of 0.05 mmol g⁻¹).



Fig. 1 The influence of nitrogen additives on oxidation of ethyl lactate in the presence of VO_x/C catalysts. Reaction conditions: Ethyl lactate 5 mmol, additives 5 mol%, VO_x/C 25 mg (0.15 mol% V relative to the substrate), 1 atm O_2 , diethyl succinate (solvent, 1 ml), 130 °C, and 4 h. The inset shows the selectivity profiles to ethyl pyruvate.

aiming to understand the effect of such additives on the aerobic oxidation of lactates.

In a typical reaction, ethyl lactate (5 mmol) and oxygen were reacted in the presence of using 25 mg of VO_x/C catalyst (0.15 mol% V relative to the substrate) in combination with different nitrogen additives. Control experiments showed that diethyl succinate is a good solvent under these conditions (see Fig. S1 in the ESI[†]). In all cases, the additive amount was kept constant at 5 mol%. Fig. 1 shows the ethyl lactate conversion profiles for three additives: pyridine, pyrrole and N-methyl pyrrole. Adding pyridine facilitated the reaction, while pyrrole and N-methyl pyrrole retarded it. Importantly, adding pyridine also increased the selectivity towards ethyl pyruvate, while with pyrrole and N-methyl pyrrole the selectivity was unchanged (see Fig. 1, inset). These effects may be related to the additives' basicity: pyridine is more basic than pyrrole, as its lone pair of electrons is not delocalized on the aromatic ring. The Lewis basicity strength pyridine > N-methyl pyrrole > pyrrole correlates with the conversion.³⁷

To examine this hypothesis further, we studied various pyridine additives bearing electron-withdrawing and electrondonating groups (Table 2). The latter were more reactive. The observed reaction rate constants (k_{obs}) in the presence of *meta*substituted pyridines were ranked $-CH_3 > -H > -Cl > -Br >$ $-NO_2$ (*cf.* entries 2–5, Table 2). *Ortho*-substituents showed similar trends (Table 2, entries 9 and 10 *vs.* entry 11).

The Hammett plot shown in Fig. 2 quantifies the *meta*-substituent effect, with ρ (reaction constant) = -2.68.^{38,39} Good correlations are obtained ($R^2 = 0.86$). This indicates that this reaction is substituent-sensitive and kinetically favored in the presence of electron-donating groups.^{40,41} There are two exceptions, namely for hydroxyl and amino substituents. The former may reflect the known tendency of phenol groups for trapping free-radicals,⁴² thus hampering the oxidation reaction (Table 2, entries 7 and 13). For the latter, the amino substituent probably can compete with the pyridine as an organic

 Table 2
 Oxidation of ethyl lactate to ethyl pyruvate in the presence of pyridine additives^a

Entry	Additive	Conversion ^b (%)	Selectivity ^b (%)	Yield (%)	$k_{\rm obs}^{\ \ c} (10^{-5} { m M h}^{-1})$
1 2	None	34 53	83 91	29 48	10.0 12.4
3	CH ₃	58	93	54	14.4
4	CI	50	87	43	11.7
5	Br	41	87	36	9.4
6	NNO ₂	36	80	29	8.3
7	N' OH	21	97	21	5.0
8	N NH ₂	16	90	14	3.6
9	CH ₃	49	92	45	11.1
10	Он	46	95	44	10.6
11		34	84	28	7.8
12		12	93	11	2.5
13	ОН	35	88	31	8.1
14	N NH ₂	6	52	3	1.4

^{*a*} Reaction conditions: Ethyl lactate 5 mmol, additive 5 mol%, VO_x/C 25 mg (0.15 mol% V relative to substrate), 1 atm O₂, diethyl succinate (solvent, 1 ml), 130 °C, and 4 h. ^{*b*} Determined by GC using biphenyl as an internal standard. ^{*c*} k_{obs} is the observed zero-order rate constant (M h⁻¹).



Fig. 2 Hammett plot for ethyl lactate oxidation over various *meta*-substituted pyridine, σ_{meta} -Hammett constant. Reaction conditions: Ethyl lactate 5 mmol, additives 5 mol%, VO_x/C 25 mg (0.15 mol% V), 1 atm O₂, diethyl succinate (solvent, 1 ml), and 4 h.

base, thereby suppressing the reaction (Table 2, entries 8, 12 and 14).

We then studied how a base additive could influence this reaction. This was performed by monitoring the initial reaction profiles over a period of 1 h and determining the selectivity and yield in the presence of various inorganic and organic bases (Table S1[†]). Plain VO_x/C gave 11% conversion and 86% selectivity to ethyl pyruvate. Inorganic Brønsted bases, with a varying pK_b of 0.2–7.9, retarded the reaction (Table S1,† entries 1-4). These bases also promoted the decomposition of ethyl pyruvate to ethanol. The organic bases piperidine, diethylamide and aniline (Table S1,† entries 6, 7 and 9), only show little advantages. Interestingly, pyridine, with its moderate pK_b of 8.8 (Table S1,[†] entry 8), gave the highest conversion (31%). Generally, the lower pK_b of nitrogen-derived organic bases represents the higher density of lone pair electron. Piperidine $(pK_{b} = 2.7)$ and diethylamide $(pK_{b} = 2.9)$ interact more strongly with ethyl lactate than pyridine (Table S1[†]). The latter probably acts as a 'catalytic shuttle'. The pyridine nitrogen first forms a moderate hydrogen-bonding with the lactate OH. Then the complex transfers to a VO_x/C active site, releasing the reactant.43 In contrast, the strong organic bases piperidine and diethylamide form a tighter lactate/base complex through strong hydrogen-bonded networks, which are less likely to release the activated ethyl lactate. This also explains why amino-substituted pyridine suppresses the activity (see Table 2). The reason that aniline had no impact on the conversion, even though its $pK_{\rm b}$ is comparable to pyridine, may be because aniline can form a Schiff base complex with the lactate carbonyl group.⁴⁴

To understand this base effect, we studied the interaction between ethyl lactate and pyridine/pyrrole compounds using density functional theory (DFT) calculations.45,46 Geometry optimization shows that both pyridine and pyrrole can form hydrogen-bonds with the hydroxyl group of ethyl lactate (Fig. S2[†]). The hydrogen bond between pyridine and ethyl lactate (1.722 Å) is shorter than that of pyrrole (2.037 Å). The interaction between ethyl lactate and pyridine is stronger than that of ethyl lactate and pyrrole by 32 kcal mol^{-1} . Actually, the hydroxyl H proton transfer is an essential step in this reaction.¹⁹ To analyse whether pyridine or pyrrole acts as proton acceptors, we calculated the joint structures of ethyl lactatepyridine (denoted as EL-pyridine) and ethyl lactate-pyrrole (EL-pyrrole) at different distances (Fig. S3[†]). We found that pyridine easily accepted the hydroxyl H of ethyl lactate, while pyrrole repelled it. This can also explain why pyrrole compounds suppressed the reaction.

The DFT results suggest that pyridine could trigger ethyl lactate dissociation *via* proton transfer. As shown in Fig. 3, this reaction proceeds through a concerted mechanism, starting from the initial reactant complex. First, the hydroxyl proton transfers to the pyridine nitrogen, forming a transition state with a relative energy of -7.2 kcal mol⁻¹ (with respect to separated reactants). Next, the carboxyl oxygen rotates towards the protonated nitrogen *via* the hydrogen bond (1.46 Å). Simultaneously, the hydroxyl oxygen moves towards the neighbouring pyridine hydrogen, giving another hydrogen bond



Fig. 3 Potential energy profile of the activation process of ethyl lactate by pyridine. The atomic configurations corresponding to the initial, transition and intermediate states.

with a length of 1.73 Å. Finally, an intermediate is produced by forming an eight-membered ring between the ethyl-propionate-2-oxide and pyridine species. In addition, the β -hydrogen of ethyl-propionate-2-oxide was also activated by pyridine: the C-H $_{\beta}$ bond stretches from 1.121 Å to 1.125 Å during this process.

From the DFT simulation, we know that pyridinic nitrogen can be protonated by ethyl lactate, facilitating the formation of a key intermediate in this reaction. To validate the simulations, we ran a series of control experiments using pyridine hydrochloride (Fig. 4). This additive should react with ethyl lactate to give a structure similar to our simulated intermediate (Fig. 4a). Indeed, adding pyridine hydrochloride gave an ethyl lactate conversion of 10% in the first 10 min, compared to 4% in the presence of pyridine and no conversion at all in the absence of an additive (Fig. 4b). The reaction rate also increased in the order: pyridine hydrochloride > pyridine \gg no additive (Fig. 4c). In another control experiment, we added both pyridine and HCl as separate additives (first the pyridine and then the acid to minimize the formation of protonated pyridine). This {pyridine + HCl} combination gave much lower conversion compared with pyridine hydrochloride (Fig. 4d), ruling out an effect of a separate Cl⁻ counter ion. These control experiments confirm that protonated pyridine plays a vital role in this reaction, in agreement with the DFT simulation results.

We then hypothesised that the ethyl lactate molecules first interact with pyridine via hydrogen bonding and only then travel to the vanadium oxide active site. To test this, we ran a series of experiments with a solid poly-4-vinylpyridine (P4VP), which can be considered as a "stationary pyridine". This was compared to its simplest homogeneous analogue, 4-methylpyridine. As shown in Fig. 5a, 4-methylpyridine gave much higher conversion than P4VP. Even after 8 h, the conversion in the presence of P4VP was <20%. This supports our hypothesis that the ethyl lactate first interacts with the pyridine, forming a complex, which travels to the vanadium oxide active site (Fig. 5b). This transfer step is hampered by the bulk polymer additive P4VP. Indeed, in the absence of any additive, VO_x/C itself can catalyze this reaction (cf. Fig. 1, no additive). Adding pyridine improves the results, but adding P4VP, which is a large polymer, retards the reaction.

Despite the diffusion barrier created by P4VP, it does show one important advantage: a high selectivity to ethyl pyruvate. We therefore reasoned that a carbonaceous support made from P4VP would combine the activity advantages of the



Fig. 4 (a) The structures of simulated intermediate and pyridine hydrochloride. (b) The time-resolved conversion profile of ethyl lactate over different additives in the presence of the VO_x/C catalyst. Reaction conditions: Ethyl lactate 5 mmol, additives 5 mol%, VO_x/C 25 mg (0.15 mol% V), 1 atm O₂, diethyl succinate (solvent, 1 ml), and 130 °C. (c) Kinetics plots for the conversion of ethyl lactate over different additives in the presence of the VO_x/C, catalyst, where C_t represents the substrate concentration at time *t* and C_o is the initial concentration. (d) Selectivity to ethyl pyruvate plotted against ethyl lactate conversion, additive: red: pyridine hydrochloride (5 mol%), black: {pyridine + HCl} (5 mol% each).



Fig. 5 (a) Plots of ethyl lactate conversion and ethyl pyruvate selectivity against reaction time; Reaction conditions: Ethyl lactate 5 mmol, additive 5 mol%, VO_x/C 25 mg (0.15 mol% V), 1 atm O₂, 130 °C, and diethyl succinate (solvent, 1 ml). (b) Proposed migratory behaviors of 4-methyl-pyridine-ethyl lactate and P4VP-ethyl lactate towards the VO_x/C catalyst.

homogeneous additive with the selectivity advantages of the heterogeneous one. This would give a stable solid oxidation catalyst without any additives.

To test this, we prepared a P4VP-supported vanadia catalyst (denoted as $VO_x/P4VP$). First, P4VP was calcined at 400 °C for 2 h under nitrogen. Then, the material was impregnated with vanadyl acetylacetonate ($VO(acac)_2$) ethanolic solutions, dried and calcined to give $VO_x/P4VP$ (Scheme 1, see the Experimental section for details). We ran X-ray photoelectron spectroscopy (XPS) experiments to identify the chemical state of nitrogen atoms of $VO_x/P4VP$. The N 1s spectra of $VO_x/P4VP$ showed a single peak, which was identical to pristine P4VP, belonging to pyridinic nitrogen at 398.5 eV (Fig. 6). This suggests that the pyridinic nitrogen atoms in $VO_x/P4VP$ are in close proximity to vanadia active sites, reducing the mass-transfer barriers.

As shown Fig. 7, the new catalyst outperformed the control combination of {4-methylpyridine + VO_x/C }. Ethyl lactate conversion over $VO_x/P4VP$ reached 84% after 8 h, compared with 69% for {4-methylpyridine + VO_x/C }. The selectivity to ethyl pyruvate was also higher (90% *vs.* 80%, respectively, see inset in Fig. 7). Note that pyridine compounds themselves can be



Scheme 1 The synthesis route of the VO_x/P4VP catalyst.



Fig. 6 XPS studies showing high resolution N 1s spectra of the pristine P4VP and VO_x/P4VP catalyst.



Fig. 7 Reaction profiles for ethyl lactate over two different catalyst systems (the inset shows the corresponding selectivity to ethyl pyruvate). Reaction conditions: Ethyl lactate 5 mmol, 1 atm O₂, diethyl succinate (solvent, 1 ml); catalyst: VO_x/P4VP 25 mg, VO_x/C 25 mg (0.15 mol% V relative to substrate) and 4-methylpyridine 5 mol%; 130 °C. Red: VO_x/P4VP catalyst, black: VO_x/C with 4-methylpyridine additive.

oxidized by vanadia.⁴⁷ In the first 4 h, the {4-methylpyridine + VO_x/C showed a higher conversion, but after 4 h, $VO_x/P4VP$ was better, most likely because the pyridinic nitrogen in the VO_x/P4VP catalyst was protected by the polymer matrix.⁴⁸ Moreover, carbon formed on the surface of VO_x/P4VP during the calcination process acts as a free-radical scavenger, slowing the undesired side oxidation of ethyl lactate.²⁸ As an added bonus, the VO_x/P4VP catalyst is easily separated by simple filtration, and can be reused at least five times without significant loss of activity (see Fig. S4[†]). A comparison of the catalytic performance of various catalysts reported previously for the liquid-phase oxidation of lactate to pyruvate is shown in Table S2.[†] Among these, Li et al. reported a novel bi-enzymatic parallel cascade system (hemoglobin-NaD⁺) for the bio-oxidation of lactate with H_2O_2 to pyruvate, giving a high selectivity of 94% with 81% yield at room temperature.49 The reaction can also be carried out with H₂O₂ as an oxidant using Ti, Pt or Pb-based catalysts (Table S2[†]). Our designed VO_x/P4VP catalyst

is among the best non-noble metal heterogeneous catalysts. It gives high yield of ethyl pyruvate with just 0.15 mol% V at 1 atm O_2 pressure.

Conclusions

Converting lactates to pyruvates can be carried out by oxidation with molecular oxygen, but obtaining high yields is a challenge. Vanadium oxides can catalyse this reaction, and the product selectivity can be increased by adding pyridine. This reaction has two key steps: complexation of the pyridine-type additive to the substrate, followed by the oxidation at the vanadium active site. In this two-step pathway, the diffusion to the active site also plays a key role. The product yield can be maximised by designing a tailor-made catalyst that takes both steps into account. This catalyst is made by first synthesising a support rich in "pyridine" groups, and then impregnating this support with vanadium sites, which are then oxidised to vanadia particles. The resulting catalyst is active and selective, giving 80% conversion with 90% selectivity to the desired product, ethyl pyruvate. It is also stable, and can be easily separated and reused multiple times without losing activity.

Experimental

Materials and instrumentation

Chemicals were obtained from commercial sources and used as received. Activated carbon (Norit® SX 1 G), ruthenium on carbon (Ru/C, Alfa Aesar, 5 wt%), platinum on carbon (Pt/C, Sigma-Aldrich, 1 wt%), poly (4-methylpyridine) (P4VP, Reillex® 402), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, VWR, \geq 96%), vanadyl acetylacetonate (VO(acac)2, Sigma-Aldrich, 98%), iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O, Sigma-Aldrich, \geq 99.95%), copper nitrate trihydrate (Cu(NO₃)₂·3H₂O, Sigma-Aldrich, \geq 99.5%), (–)–ethyl L-lactate (Sigma-Aldrich, \geq 98.0%), diethyl succinate (Sigma-Aldrich, 99%), and all other pyridine-derived chemicals were purchased from Sigma-Aldrich. Gas chromatography (GC) analysis was performed by using an Agilent 7820A instrument equipped with a flame ionization detector (FID), autosampler (G4513A) and a dimethylpolysiloxane capillary column (VB-1, 30 m \times 0.32 mm \times 3.00 μ m). The metal loading was measured by inductively coupled plasma (ICP) atom emission spectroscopy (AES) on a Thermo IRIS Intrepid II XSP. XPS spectra were collected using a Thermo Scientific K-ALPHA with Al-K radiation. S-shaped background subtraction and fitting the experimental curve to a combination of a Lorentzian (30%) and Gaussian (70%) lines were performed. Binding energies (BE), referenced to the C 1s line at 284.6 eV, have an accuracy of ±0.1 eV.

Procedure for carbon supported metal oxide (MO_x/C) preparation

The MO_x/C catalysts were prepared following the procedure reported by Srinivas *et al.*⁵⁰ Example: VO_x/C . 5.0 grams of acti-

vated carbon was added into 50 ml ethanol solution by stirring for 30 min in a 250 ml round bottomed flask at room temperature. Subsequently, 1.5 mmol vanadyl acetylacetonate (VO (acac)₂) was added to the solution and stirred at 80 °C overnight. After ethanol evaporation, the solid was continually dried at 100 °C for 12 hours, then ground by using a mortar and pestle to a fine powder and followed by temperature-programmed heat-treatment at 400 °C for 2 h, with a heating rate of 2 °C min⁻¹ under a nitrogen flow. The catalysts CoO_x/C , CuO_x/C and FeO_x/C were similarly prepared from the respective precursors $Co(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and Fe $(NO_3)_3 \cdot 9H_2O$.

Procedure for P4VP-supported vanadia preparation (VO_x/P4VP)

In a typical synthesis of the VO_x/P4VP catalyst, 10 grams P4VP was transferred into a quartz boat with a quartz cover, and then wrapped using aluminum foil. The sealed P4VP was calcined at 400 °C for 2 h under nitrogen at a heating rate of 1 °C min⁻¹ and then cooled to room temperature. Then, 1 gram of the resulting black powder was ultrasonically dispersed into 50 ml ethanol solution. Next, 0.3 mmol vanadyl acetylacetonate (VO(acac)₂) was added to the mixture by stirring at 80 °C overnight in a 250 ml round bottomed flask. Then the solid was ground by using a mortar and pestle to fine powder, and subsequent calcination at 400 °C for 2 h under nitrogen, with a heating rate of 2 °C min⁻¹ in a nitrogen flow was performed.

Procedure for catalyst testing

In a typical reaction, ethyl lactate (5 mmol), additive (5 mol%, relative to the substrate), catalyst (25 mg) and diethyl succinate (1 ml, solvent) were added into a 25 ml flask equipped with a dioxygen balloon. The reaction mixture was heated to 130 °C under magnetic stirring (800 rpm). After reaction, the flask was cooled to room temperature. Next, the product was filtered using 0.45 μ m PTFE syringe filters. Then, the filtrate was directly analysed by GC by adding biphenyl (50 mg) as an internal standard.

Density functional theory (DFT) calculations

DFT calculations were performed using the CP2K software package, which uses the combined Gaussian and plane-wave (GPW) method for the calculation of forces and energies.⁵¹ The valence orbitals were described by the DZVP-GTH Gaussian basis set, all calculations were carried out using the PBE density functional augmented with the Grimme D3 dispersion correction.⁴⁶ The plane wave kinetic energy cutoff was set to 400 eV. We used the DIMER method to identified the transition states.⁵² The adsorption energies were defined as $\Delta E = E_{\text{total}} - E_{\text{ethyl lactate}} - E_{\text{pyridne/pyrrole}}$, where $E_{\text{ethyl lactate}}$, $E_{\text{pyridne/pyrrole}}$, and E_{total} refer to the energies of the free ethyl lactate, pyridine /pyrrole, and complex system, respectively.⁵³

Conflicts of interest

There are no conflicts to declare.

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