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Understanding the oxidative dehydrogenation of ethyl lactate to ethyl pyruvate over vanadia/titania†

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We studied the vapour-phase oxidative dehydrogenation (ODH) of ethyl lactate with air to give ethyl pyruvate over V2O5/TiO2 catalysts in a fixed-bed reactor. The nature of the vanadia species is changed by varying the vanadium surface density, and the corresponding structure of the VOx species was determined by XRD, UV-vis spectroscopy, XPS and H2-TPR. Monomeric and isolated vanadia species dominate at lower vanadium surface densities. As the surface density increases, two-dimensional polyvanadates and bulk-like vanadia crystallites become predominant. The activity per vanadium decreases with increasing vanadium surface density, indicating that the monomeric VOx species is better for pyruvate production and that the V–O–Ti bonds play an important role in the ODH of ethyl lactate. This is also confirmed by the superior catalytic performance of V2O5/TiO2 compared to vanadium supported on MgO, Al2O3, ZrO2 and CeO2.

In situ DRIFT spectroscopy coupled with mass analysis shows that the reaction can involve three possible adsorption modes of ethyl lactate on the V2O5/TiO2 surface. Under anaerobic conditions, 2-hydroxypropionate forms, giving ethyl acetate as the major product. Conversely, under aerobic conditions, oxygen that is chemisorbed on V2O5/TiO2 is active and easily replenished from the gas phase, converting the ethyl-propionate-2-oxide intermediate into ethyl pyruvate.

Introduction

Lignocellulosic biomass is one of the few sources of truly renewable carbon. But there’s a lot of it: even today, the world biomass production could meet the entire carbon demand of the chemical industry (excluding transportation fuels). Typically, biomass is first converted into simple derivatives, or ‘platform molecules’, that are then reacted further to industrial chemicals. Lactic acid (LA) and lactic esters are important platform molecules. They can be converted into a variety of bulk chemicals, including acrylic acid, propionic acid, pyruvic acid and acetaldehyde (Scheme 1).

The oxidative dehydrogenation (ODH) of lactic acid to pyruvic acid is especially interesting due to the high demand for pyruvates in the pharmaceutical and agrochemical sectors. Today, pyruvates are still made via the classic dehydrative decarboxylation of tartaric acid in the presence of an excess of KHSO4. However, the extra reagent and the high temperature (300 °C) make this process unsustainable. Therefore, attention has focused on oxidative dehydrogenation of lactate as a ‘greener’ alternative. Several catalysts including Pd/Pt,9 iron phosphates,10 metal oxides (Mo, Ti, Zr, W and Sn),11 and binary oxides (TeO2–MoO3, SnO2–MoO3)12,13 were reported for this reaction in both the gas phase and liquid phase. Yet most of these also catalyse C–C scission, especially in the gas phase, giving acetaldehyde, CO and CO2. The catalytic challenge, therefore, is running a selective ODH reaction at a lower temperature, thus avoiding C–C bond scission. Supported/bulk vanadium oxides are used in a variety of ODH reactions at relatively low temperatures.14,15 The performance of supported vanadium catalysts depends on the type of support and the structure of the surface vanadium species. Compared with other oxide supports, titania interacts strongly with vanadia. The anatase phase in particular gives a stable VOx monolayer with a catalytic oxidation...
performance superior to that of rutile.\textsuperscript{17,18} We recently showed that TiO\textsubscript{2} itself can also catalyse the ODH of ethyl lactate to ethyl pyruvate in the liquid phase, due to its high affinity to ethyl lactate and oxygen.\textsuperscript{19} Meanwhile, Li \textit{et al.} reported that MoVNbO\textsubscript{x} supported on TiO\textsubscript{2} was more active than unsupported components for vapour phase ethyl lactate conversion.\textsuperscript{20} Cavani and co-workers elucidated the role of the components in MoV(Nb)TeO catalysts, showing that vanadium is crucial for achieving high ODH performance.\textsuperscript{21} Our preliminary tests showed that commercial V\textsubscript{2}O\textsubscript{5} gave higher yields of pyruvate compared with other oxides (MoO\textsubscript{3}, TeO\textsubscript{2} and MoVO\textsubscript{x}) at low temperatures (Fig. S1\textsuperscript{†}). Thus, we hypothesised that VO\textsubscript{x}/TiO\textsubscript{2} would be both active and selective in the ODH of lactates.

Here, we studied the structure–activity relationships in ethyl lactate ODH over V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} catalysts. We prepared a series of vanadium oxides supported on anatase titania, varying the vanadium loading \textit{via} incipient wetness impregnation. Catalyst characterisation showed that different types of VO\textsubscript{x} species (monomeric, polymeric, and crystalline domains) formed on the TiO\textsubscript{2} surface. We then examined the correlation between the VO\textsubscript{x} structure and catalytic activity in the ODH of ethyl lactate with air in a fixed-bed reactor, comparing the catalytic properties of V\textsubscript{2}O\textsubscript{5} impregnated on TiO\textsubscript{2}, MgO, Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2} and CeO\textsubscript{2}. Across this series, V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} showed a superior ODH activity, which we attribute to the cooperative effects between vanadia and titania. \textit{In situ} DRIFT spectroscopy showed that three adsorption modes of ethyl lactate are possible on the V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} surface. Under anaerobic conditions, 2-hydroxypropionate forms, giving ethyl acetate as the major product. Under aerobic conditions, oxygen chemisorbed on V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} is active and easily replenished from the gas phase, converting the ethyl-propionate-2-oxide intermediate into ethyl pyruvate.

**Results and discussion**

**Synthesis and characterization of VO\textsubscript{x}/TiO\textsubscript{2} catalysts**

First, we prepared five supported vanadium oxide catalysts by incipient wetness impregnation using aqueous solutions of ammonium metavanadate (NH\textsubscript{4}VO\textsubscript{3}) and oxalic acid, which were subsequently dried and calcined at 550 °C. The samples are denoted as \(n\)-V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}, where \(n\) represents the wt% of V\textsubscript{2}O\textsubscript{5} on TiO\textsubscript{2} (\(n\) = 1%, 3%, 5%, 10%, 20%; see the Experimental section for details).

We then studied the textural properties of the catalysts using nitrogen adsorption–desorption isotherms. All samples showed a superior ODH activity, which we attribute to the cooperative effects between vanadia and titania. \textit{In situ} DRIFT spectroscopy showed that three adsorption modes of ethyl lactate are possible on the V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} surface. Under anaerobic conditions, 2-hydroxypropionate forms, giving ethyl acetate as the major product. Under aerobic conditions, oxygen chemisorbed on V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} is active and easily replenished from the gas phase, converting the ethyl-propionate-2-oxide intermediate into ethyl pyruvate.

**Scheme 1** Lactic acid can be converted into a variety of important bulk chemicals.

**Fig. 1** X-ray diffraction patterns of VO\textsubscript{x}/TiO\textsubscript{2} catalysts with different loadings of V\textsubscript{2}O\textsubscript{5}: (a) pristine TiO\textsubscript{2}, (b) 1-V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}, (c) 3-V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}, (d) 5-V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}, (e) 10-V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} and (f) 20-V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}.

**Fig. 2** Scanning electron micrographs of VO\textsubscript{x}/TiO\textsubscript{2} catalysts: (a) 1-V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}, (b) 3-V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}, (c) 5-V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} and (d) 10-V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}.
showed a type IV isotherm with an H1-type hysteresis loop characteristic of mesoporous materials (Fig. 3). As expected, increasing the V content lowered the BET surface area from 81 m\(^2\) g\(^{-1}\) to 51 m\(^2\) g\(^{-1}\) (Table 1). Actually, the structure of surface VO\(_x\) species depends closely on the vanadium surface density (V\text{atoms} \text{nm}^{-2}). The surface densities of our samples are 0.8, 3.0, 4.8 and 12.8 V\text{atoms} \text{nm}^{-2}, corresponding to a V\(_2\)O\(_5\) content of 1, 3, 5 and 10 wt\%, respectively. The theoretical surface density value for monovanadate is 2–3 V\text{atoms} \text{nm}^{-2}.\(^{15}\) Thus, the vanadia species of 1-V\(_2\)O\(_5\)/TiO\(_2\) and 3-V\(_2\)O\(_5\)/TiO\(_2\) are probably isolated VO\(_4\) species, while 5-V\(_2\)O\(_5\)/TiO\(_2\) and 10-V\(_2\)O\(_5\)/TiO\(_2\) are predominantly polymeric VO\(_4\) species and V\(_2\)O\(_5\) crystallites.\(^{23,24}\)

To confirm the coordination environment of the vanadium species, we used UV-visible diffuse reflectance spectroscopy (UV-vis DRS, see Fig. 4A). The absorption intensity in the visible region is enhanced after depositing vanadium oxide on the titania support. 1-V\(_2\)O\(_5\)/TiO\(_2\) showed charge-transfer bands centred around 280–350 nm, which are assigned to isolated tetrahedral V\(^{5+}\) species.\(^{25}\) As the V\(_2\)O\(_5\) loading increased, the absorption bands shifted to higher wavelengths, reflecting the lower-energy transitions of the charge transfer between oxygen and V atoms.\(^{26}\) This indicates the formation of highly coordinated polymeric vanadium species from isolated tetrahedral monomeric species (cf. the similar structures observed for molybdenum\(^{27}\)). Increasing the vanadia content to 10 wt\% showed crystalline V\(_2\)O\(_5\) species (absorption at 490 nm\(^\text{28,29}\)). Defining the position of isolated and polymerized VO\(_4\) units using UV-vis DRS is difficult, as their absorption bands can overlap with the strong absorption of the titania support.\(^{30}\) However, the absorption edge energy (\(E_g\)) can give quantitative information on the coordination number and the local structure of VO\(_x\) species. The \(E_g\) value is determined by finding the intercept on the \(X\)-axis of the tangent line in the low-energy rise of the plot of [\(F(R_\alpha)h\nu\)]\(^{1/2}\) vs. \(h\nu\), where \(F(R_\alpha)\) is the Kubelka–Munk function and \(h\nu\) is the incident photon energy.\(^{31}\) The corresponding \(E_g\) values for V\(_2\)O\(_5\)/TiO\(_2\) are shown in Fig. 4B, wherein the value of pure TiO\(_2\) is about 3.27 eV. For the V\(_2\)O\(_5\)/TiO\(_2\) catalysts, the \(E_g\) value gradually decreases with increasing surface vanadia content from 3.19 to 2.1 eV. A similar trend was observed by Danilevich et al.\(^{32}\) The high \(E_g\) value at low vanadium surface density corresponds to isolated surface VO\(_4\) species. When the vanadium content is 1\%, \(E_g \approx 3.19\) eV, which is close to the value of 3.21 eV for Na\(_3\)VO\(_4\) (where vanadium exists as an isolated tetrahedral VO\(_4\) species).\(^{33}\) Bulk NaVO\(_3\) was reported to have a polymeric tetrahedral VO\(_4\) structure with an \(E_g\) value of

![Fig. 3](image-url) Nitrogen adsorption–desorption isotherms of VO\(_x\)/TiO\(_2\) catalysts. (a) Pristine TiO\(_2\), (b) 1-V\(_2\)O\(_5\)/TiO\(_2\), (c) 3-V\(_2\)O\(_5\)/TiO\(_2\), (d) 5-V\(_2\)O\(_5\)/TiO\(_2\) and (e) 10-V\(_2\)O\(_5\)/TiO\(_2\). The isotherms in the figure are shifted up for the sake of clarity.

![Fig. 4](image-url) (A) UV-vis absorption spectra of TiO\(_2\), V\(_2\)O\(_5\) and V\(_2\)O\(_5\)/TiO\(_2\) catalysts. (B) [\(F(R_\alpha)h\nu\)]\(^{1/2}\) plotted against the energy of the incident photon for the determination of edge energy for V\(_2\)O\(_5\)/TiO\(_2\) catalysts; the inset shows the corresponding \(E_g\) values. The edge energies are determined from the intercept on the \(X\)-axis of a straight line fitted through the rise of the function [\(F(R_\alpha)h\nu\)]. (C) Schematic structures of V\(_2\)O\(_5\)/TiO\(_2\) catalysts showing different types of vanadia species.

<table>
<thead>
<tr>
<th>Sample</th>
<th>V content(^a) (ICP, wt%)</th>
<th>V surface density (VO(_4)/nm(^2))</th>
<th>(S_{\text{BET}})(^b) (m(^2) g(^{-1}))</th>
<th>(V_p)(^b) (cm(^3) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure TiO(_2)</td>
<td>—</td>
<td>—</td>
<td>81.3</td>
<td>0.50</td>
</tr>
<tr>
<td>1-V(_2)O(_5)/TiO(_2)</td>
<td>0.58</td>
<td>0.8</td>
<td>81.2</td>
<td>0.52</td>
</tr>
<tr>
<td>3-V(_2)O(_5)/TiO(_2)</td>
<td>1.80</td>
<td>3.0</td>
<td>70.9</td>
<td>0.51</td>
</tr>
<tr>
<td>5-V(_2)O(_5)/TiO(_2)</td>
<td>2.70</td>
<td>4.8</td>
<td>66.3</td>
<td>0.49</td>
</tr>
<tr>
<td>10-V(_2)O(_5)/TiO(_2)</td>
<td>5.64</td>
<td>12.8</td>
<td>51.8</td>
<td>0.43</td>
</tr>
</tbody>
</table>

\(^a\) Determined by ICP analysis. \(^b\) Calculated based on N\(_2\) sorption at 77 K.
2.41 eV. Thus, we assume that the 3\% V_2O_5 on TiO_2 (with E_g = 2.84 eV) also contains polymerized VO_4 units in addition to isolated VO_4 species. Increasing the V_2O_5 content to 5\% yielded an E_g value of 2.38 eV, indicating the presence of a higher amount of polyvanadate species. Note that the E_g value of 10\% V_2O_5/TiO_2 (2.10 eV) is close to that of bulk V_2O_5 (2.05 eV), suggesting that the polymerized VO_4 species is aggregated to crystalline V_2O_5, in agreement with the XRD results.

We ran H_2-TPR experiments to further elucidate the oxidation state of surface vanadia species and the reducibility of V_2O_5/TiO_2 catalysts (see Fig. 5). The pristine TiO_2 support showed only a very weak peak around 540 °C. After depositing vanadia, the temperature of the maximum hydrogen consumption (T_max) shifted to a lower value, compared with pure V_2O_5. This suggests that V_2O_5/TiO_2 is easier to reduce than pure TiO_2 or V_2O_5. Among our V_2O_5/TiO_2 catalysts, the T_max shifted to a higher temperature with increasing V_2O_5 content. Generally, the reducibility of supported V_2O_5 catalysts is affected both by the type of surface vanadia species and vanadium coverage. Indeed, polymeric VO_2 species in the monolayer are reported to be more easily reduced than monomeric ones. In our case, the 3-V_2O_5/TiO_2 sample, which also contains polymerized VO_4 units, was more easily reduced compared to the 1-V_2O_5/TiO_2 sample, which has only monomeric VO_4 species, in agreement with published data. VO_x species below or at monolayer coverage are more reducible than the VO_x species in multilayers and in crystalline or bulk vanadia. Accordingly, reducing 5-V_2O_5/TiO_2 and 10-V_2O_5/TiO_2 was even more difficult, in agreement with this trend.

We then ran X-ray photoelectron spectroscopy (XPS) measurements to identify the chemical species on the surface (see Fig. 6). The V 2p (Fig. 6a) was deconvoluted into two distinct peaks centered at 516.5 eV and 517.5 eV, corresponding to V^{4+} and V^{5+} species, respectively. The peaks at 464.7 eV and 458.9 eV are assigned to Ti 2p_3/2 and Ti 2p_1/2 (Fig. 6b), suggesting that the Ti^{4+} state predominates. Similarly, the spectra of O 1s (Fig. 6c) were fitted with three peaks. The main peak was observed at a lower BE of 530.2 eV and assigned to lattice oxygen species (O_{latt}). The peak at around 531.7 eV represented the surface chemisorbed oxygen (O_{chem}), while that at 532.6 eV represented the chemisorbed water O_{H_2O}.

Catalytic activity

We first analysed the mass-transfer limitations for the oxidative dehydrogenation of ethyl lactate with air over 3-V_2O_5/TiO_2 catalysts in a fixed-bed reactor. For studying intra-particle diffusion limitations, we ran a series of experiments varying the catalyst particle sizes from 20 to 80 mesh. As shown in Fig. S2†, the ethyl lactate conversion remained constant, ruling out the internal diffusion limitations. The external diffusion limitation was also examined by changing the ethyl lactate feed rate and the catalyst amount. Here we varied the catalyst amount (W) as 0.5 g, 1 g, 1.5 g and 2 g (Fig. S3†) and for each catalyst weight, we changed the flow rate (F). The plot of ethyl lactate conversion against W/F (Fig. S3†) shows that the curves are similar, indicating the absence of external diffusion limitations.

Then we studied the effect of reaction temperature on the ODH of ethyl lactate over 3-V_2O_5/TiO_2 (Fig. S4†). The ethyl lactate conversion increased from 60\% to 95\% when the reaction temperature was raised from 160 °C to 340 °C. The high temperature facilitated the undesired side reactions. The optimal temperature is about 180 °C, which gave the highest pyruvate selectivity of 80\%. Fig. S4† also shows the change in product selectivity at different temperatures. At low temperatures (below 200 °C), ethanol was the main by-product due to the hydrolysis of ethyl lactate. Minor by-products such as acetaldehyde and acetic acid were also detected. Additionally, acrylate (acrylic acid and ethyl acrylate) and propionate (propionic acid/ethyl propionate) were formed with increasing temperature, reaching a selectivity of 15\% and 18\%, respectively, at 340 °C. This indicates that dehydrogenation and dehydration occur at high temperatures, in line with previous reports.

We also varied the liquid hourly space velocity (LHSV) of ethyl lactate from 0.5 h^{-1} to 3.5 h^{-1} (corresponding to a 1–8 ml h^{-1} ethyl lactate feeding rate). The results are summarized in Table S1.† As expected, with an increase in LHSV, the ethyl lactate conversion gradually decreased due to the decrease in contact time. The ethyl pyruvate selectivity...
increased from 20% to 80% with the change in LHSV from 0.5 to 2.5 h⁻¹. However, a further increase in LHSV did not favor pyruvate. This is probably due to the coverage of the active sites of the catalyst by the reactants, leading to coke formation.

Then, the activities of V₂O₅/TiO₂ catalysts for the ODH reaction of ethyl lactate to ethyl pyruvate were investigated. The pure anatase TiO₂ support gave only low yields. Similarly, control experiments with commercial bulk V₂O₅ gave <30% pyruvate. Interestingly, even 1-V₂O₅/TiO₂ gave a higher selectivity and yield than bulk V₂O₅ (Fig. 7). Note that the specific surface area of 1-V₂O₅/TiO₂ is 81 m² g⁻¹, which is much higher than that of V₂O₅ (5 m² g⁻¹). This suggests that highly dispersed vanadia is responsible for the catalytic activity. When the vanadium loading was increased to 3%, the selectivity to pyruvate reached a maximum of 78% at 62% conversion. Increasing the V loading further did not improve the catalytic performance. To better differentiate the influence of surface vanadia species on catalytic performance, control experiments were performed by increasing the LHSV and decreasing the air flow at low reaction temperatures (160 °C, 180 °C vs. 200 °C). Fig. 8 shows that all V₂O₅/TiO₂ catalysts show higher ethyl lactate conversion than pure TiO₂ and V₂O₅. The sub-monolayer 1-V₂O₅/TiO₂ catalyst gave 10% ethyl lactate conversion at 160 °C. Increasing the vanadia loading to 3% (near monolayer coverage) gave an ethyl lactate conversion of 28%. With a vanadia content of over 3%, the conversion almost levelled up. We therefore attribute the reactivity enhancement to non-polymeric vanadium species close to TiO₂.

To further evaluate the catalytic performance of V₂O₅/TiO₂, we calculated the turnover frequency (TOF) under a relatively low conversion of ethyl lactate, and the results are shown in Fig. 9. The TOF of V₂O₅/TiO₂ was inversely proportional to the vanadium surface density, in close correlation with the absorption edge energy (E_g, see the right axis in Fig. 9). A low V surface density with high E_g, where vanadium is present as monomeric species, gave the highest TOF. As the VO₂ surface density increases, isolated VO₂ species agglomerate with their nearest neighbours, resulting in a lower ratio of V–O–Ti bonds and an increase in V–O–V and V≡O bonds. Meanwhile, the V–O–Ti bonds within multilayers are less accessible than those in the surface monolayer, which may explain the lower selectivity at higher vanadium loadings. Ji et al. reported that the ratios of V⁴⁺/(V⁴⁺ + V⁵⁺) reflected the ratio [(vanadium strongly interacting with the support)/(total vanadium)]; in our case, the V loading increased from 1% to 10%, while the ratios of V⁴⁺/(V⁴⁺ + V⁵⁺) decreased from 0.5 to 0.29 (Table S2†). This result confirms the decrease in V–O–Ti bonds. Earlier, Wachs et al. showed that the reactivity of VO₂ species is unrelated to the terminal V≡O bonds in the partial oxidation of methanol. Oxygen labelling experiments also demonstrated that the V≡O bond is stable during butane oxidation.48,49 In our system, the terminal V≡O bonds do not favour the TOF of ethyl lactate conversion, as we showed subsequently using DRIFTS study. The fact that the 1-V₂O₅/TiO₂ catalyst, which has negligible V–O–V bonds, gave comparable catalytic activity, confirms that the bridging V–O–V bond...
does not play a role in our reaction. For comparison, we prepared a mixture of \( \text{V}_2\text{O}_3 \) and \( \text{TiO}_2 \) by mixing bulk \( \text{V}_2\text{O}_5 \) and \( \text{TiO}_2 \) powder in a mortar. This physical mixture, which contained 3 wt% \( \text{V}_2\text{O}_5 \), gave only a yield of 5.6% ethyl pyruvate, compared to the 48.1% yield obtained over impregnated \( \text{V}_2\text{O}_5/\text{TiO}_2 \) (with the same vanadium loading and under otherwise identical reaction conditions). Thus, we concluded that the catalytic performance is determined by the structure of surface vanadium species, and in particular, the O–O–Ti bonds play a critical role in the oxidative dehydrogenation of ethyl lactate.

Three types of bonds can be present in supported vanadia catalysts: V≡O, V–O–V and V–O–M (where M is the support metal cation). To understand the importance of the V–O–M bonds, we studied vanadium oxide catalysts supported on four different supports: \( \text{MgO}, \text{Al}_2\text{O}_3, \text{ZrO}_2 \) and \( \text{CeO}_2 \), varying the support surface acidity.50 For a fair comparison of V species, we prepared porous supports with a high surface area and subsequently impregnated 1 wt% of vanadium oxide on each support to form isolated \( \text{VO}_x \) species (see the Experimental section for details). The acidity of oxide supports is a key factor in many ODH systems.52 The relative acidity in this series is \( \text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{ZrO}_2 > \text{CeO}_2 > \text{MgO} \).53,54 In each case, we first tested the support alone in our reaction at 180 °C. Only \( \text{MgO} \) showed some conversion (13%) but no selectivity (because ethyl lactate undergoes hydrolysis to ethanol and lactic acid on the basic \( \text{MgO} \) surface). After introducing vanadia, the catalytic activities of the supported vanadia catalysts are summarized in Table 2. After impregnation, the reactivity of \( \text{V}_2\text{O}_5/\text{MgO} \) was unchanged. Conversely, the catalyst supported on acidic \( \text{Al}_2\text{O}_3 \) showed high conversion but low selectivity, owing to a competing decarboxylation of ethyl pyruvate to acetaldehyde.13 \( \text{TiO}_2 \)-supported vanadium oxide showed the highest catalytic activity, while \( \text{V}_2\text{O}_5/\text{ZrO}_2 \) and \( \text{V}_2\text{O}_5/\text{CeO}_2 \) scarcely catalyzed the reaction under identical conditions. Fig. 10 shows the Arrhenius plots of ethyl lactate consumption rates. For \( \text{V}_2\text{O}_5/\text{TiO}_2 \), the apparent activation energy \( (E_a) \) of ethyl lactate conversion (48 kJ mol\(^{-1}\)) is lower than that of \( \text{V}_2\text{O}_5/\text{Al}_2\text{O}_3 \) (57 kJ mol\(^{-1}\)), \( \text{V}_2\text{O}_5/\text{ZrO}_2 \) (75 kJ mol\(^{-1}\)) and \( \text{V}_2\text{O}_5/\text{CeO}_2 \) (127 kJ mol\(^{-1}\)). These results confirmed that the monomeric V–O–Ti species is more catalytically active, confirming further the importance of the vanadium–oxygen interactions.

**Table 2.** ODH of ethyl lactate to ethyl pyruvate over \( \text{V}_2\text{O}_5 \) on various supports*

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>( S_{\text{BET}} ) (m(^2) g(^{-1}))</th>
<th>Con. (%)</th>
<th>Sel. (%)</th>
<th>Yield (%)</th>
<th>Surface pH*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-V(_2\text{O}_5)/CeO(_2)</td>
<td>50</td>
<td>1</td>
<td>32.2</td>
<td>Trace</td>
<td>6.75</td>
</tr>
<tr>
<td>2</td>
<td>1-V(_2\text{O}_5)/MgO</td>
<td>198</td>
<td>15.9</td>
<td>0.5</td>
<td>Trace</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>1-V(_2\text{O}_5)/ZrO(_2)</td>
<td>89</td>
<td>28.5</td>
<td>43.9</td>
<td>12.5</td>
<td>5.9–6.1</td>
</tr>
<tr>
<td>4</td>
<td>1-V(_2\text{O}_5)/Al(_2\text{O}_3)</td>
<td>278</td>
<td>35.6</td>
<td>36.7</td>
<td>13.1</td>
<td>8.9</td>
</tr>
<tr>
<td>5</td>
<td>1-V(_2\text{O}_5)/TiO(_2)</td>
<td>81</td>
<td>58.7</td>
<td>63.7</td>
<td>37.4</td>
<td>6.0–6.4</td>
</tr>
</tbody>
</table>

* Reaction conditions: 5 ml h\(^{-1}\) ethyl lactate, 2.25 L h\(^{-1}\) air flow (molar ratio of ethyl lactate/O\(_2\) = 2.3), 1.0 g catalyst (1 wt% of metal oxide on TiO\(_2\)), 180 °C. Calculated based on N\(_2\) sorption at 77 K. Determined by GC using biphenyl as an external standard. Based on ref. 50 and 51.

**Fig. 10.** Arrhenius plots for steady-state ethyl lactate conversion over supported \( \text{V}_2\text{O}_5 \) catalysts. Reaction conditions: LHSV = 4 h\(^{-1}\), air flow = 1 L h\(^{-1}\). Ethyl lactate consumption rate:

\[
\frac{r_{\text{ethyl lactate}}}{\text{mass of catalyst}} = \frac{\text{moles of ethyl lactate per hour in the reactor (mol s}^{-1}\text{)}}{\text{mol s}^{-1}}
\]

The apparent activation energy \( (E_a) \) was measured at a series of temperatures under 20% ethyl lactate conversion.

**In situ DRIFTS study.** Further insight into the reaction can be gained by *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Fig. 11 shows the *in situ* DRIFTS of temperature-programmed ethyl lactate desorption on 3-V\(_2\text{O}_5/\text{TiO}_2 \) in the absence of oxygen. The characteristic bands of ethyl lactate adsorbed on \( \text{V}_2\text{O}_5/\text{TiO}_2 \) were detected. The C–H vibrations were observed at 2990 cm\(^{-1}\), 2940 cm\(^{-1}\), 2883 cm\(^{-1}\), 1454 cm\(^{-1}\), 1387 cm\(^{-1}\) and 1302 cm\(^{-1}\), and ascribed to \( v_{\text{as}}(\text{CH}_3) \), \( v(\text{C–H}) \), \( \delta_{\text{as}}(\text{CH}_3) \), \( \delta(\text{CH}_3) \) and \( \delta(\text{C–H}) \), respectively.55,56 Increasing the temperature broadened these carbonyl and carboxyl peaks, and the signals of \( v(\text{CO}) \) and \( v_{\text{as}}(\text{CO}) \) were blue-shifted to 1540 cm\(^{-1}\) and 1445 cm\(^{-1}\) over 250 °C. This is because of the formation of adsorbed acetate species.57 Evidently, we detected ethyl acetate by monitoring the mass signals during the temperature-programmed ethyl lactate desorption (Fig. S6†). The C=O stretching of ethyl lactate weakened (1730 cm\(^{-1}\) and 1667 cm\(^{-1}\)), accompanying two new shoulder peaks at 1780 cm\(^{-1}\) and 1566 cm\(^{-1}\) and 1420 cm\(^{-1}\), assigned to \( v(\text{C–O}) \), \( v(\text{C–O·M}) \), \( v(\text{COO}) \) and \( v_{\text{as}}(\text{COO}) \) vibrations, respectively.55,56 Increasing the temperature broadened these carbonyl and carboxyl peaks, and the signals of \( v(\text{COO}) \) and \( v_{\text{as}}(\text{COO}) \) were blue-shifted to 1540 cm\(^{-1}\) and 1445 cm\(^{-1}\) over 250 °C. This is because of the formation of adsorbed acetate species.60 Evidently, we detected ethyl acetate by monitoring the mass signals during the temperature-programmed ethyl lactate desorption (Fig. S6†). The C=O stretching of ethyl lactate weakened (1730 cm\(^{-1}\) and 1667 cm\(^{-1}\)), accompanying two new shoulder peaks at 1780 cm\(^{-1}\) and 1561 cm\(^{-1}\). These bands were assigned to the carboxyl stretching of the \( \alpha \)-keto group of the pyruvate, supporting the experimental results (Fig. S5†). The surface chemisorbed oxygen of \( \text{V}_2\text{O}_5/\text{TiO}_2 \) could participate in the oxidation of lactate without molecular oxygen. The bands at 1224 cm\(^{-1}\) and 1141 cm\(^{-1}\) may reflect the alcohol OH related C–O stretching vibrations of ethyl lactate.61

Analysis of the DRIFT spectra shows several possible adsorption modes of ethyl lactate on the catalyst surface...
The main features are the vibration differences of C–O, carbonyl (C=O) and carboxyl (COO) groups. The three adsorption modes (a), (b) and (c) were detected in line with published data, while mode (d) was not detected. The weak band at 1271 cm$^{-1}$ can be attributed to the O–H stretch of mode (c). Considering that mode (c) has no carbonyl stretching signals, modes (a) and (b) dominate at low temperature. The mass signals of both ethanol and CO$_2$ increased with temperature (Fig. S6†), due to the decomposition process. This agrees well with the changes of in situ DRIFTS.

We also conducted in situ DRIFTS experiments on ethyl lactate adsorbed on 3-V$_2$O$_5$/TiO$_2$ with O$_2$. As shown in Fig. 12, the vibrational bands of ethyl lactate on the catalyst were similar to the spectra at low temperatures (cf. Fig. 11).

Table 3. Ethyl lactate adsorption modes and their characteristic vibration wavenumber

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Vibrational mode</th>
<th>Wavenumber$^a$ (cm$^{-1}$)</th>
<th>Wavenumber$^b$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>v(C=O)</td>
<td>1725</td>
<td>1730</td>
</tr>
<tr>
<td></td>
<td>v(C=O)</td>
<td>1668</td>
<td>1667</td>
</tr>
<tr>
<td></td>
<td>v$_{as}$(COO)</td>
<td>1569</td>
<td>1566</td>
</tr>
<tr>
<td></td>
<td>v$_{as}$(COO)</td>
<td>1450</td>
<td>1420</td>
</tr>
<tr>
<td></td>
<td>v(C–O)</td>
<td>1058</td>
<td>Not detected</td>
</tr>
<tr>
<td></td>
<td>v(C–O)</td>
<td>1118</td>
<td>Not detected</td>
</tr>
<tr>
<td></td>
<td>v(C–O)</td>
<td>1614</td>
<td>Not detected</td>
</tr>
</tbody>
</table>

AL = Alcoholic functionalities. $^a$ Based on ref. 55 and 56. $^b$ From our in situ DRIFTS.
still present at 400 °C in the presence of carbonates. These observations support the hypothesis that V=O bonds are not involved in the ODH of ethyl lactate while V–O ones play a key role in the reaction.

In Fig. 13, we propose a reaction network for the aerobic and anaerobic conversion of ethyl lactate. Ethyl lactate first absorbs and dissociates on the V₂O₅/TiO₂ surface, with adsorption modes (a), (b) and (c). Modes (a) and (b) dominate at low temperatures, while model (c) generates 2-hydroxypropionate on the surface through a hydrolysis process at higher temperatures. In the absence of molecular oxygen, increasing the temperature accelerates the formation of mode (c), subsequently giving ethyl acetate as the major product. Pyruvate species can also be produced but are limited by the surface chemisorbed oxygen. Under aerobic conditions, however, molecular oxygen reoxidizes the catalyst, replenishing the surface oxygen and promoting the oxidative dehydrogenation of ethyl lactate to ethyl pyruvate.

**Conclusions**

We studied the catalytic oxidative dehydrogenation of ethyl lactate to ethyl lactate over V₂O₅/TiO₂ catalysts. To explore the structure–activity relationship for various vanadia species, a series of V₂O₅/TiO₂ catalysts with different surface densities were prepared via incipient wetness impregnation. As their surface density increases, the isolated VOₓ species agglomerate into polymeric and crystalline VOₓ species, leading to a decrease in TOF of ethyl lactate oxidation. The titania-supported vanadium oxide was superior to vanadia catalysts supported on MgO, Al₂O₃, ZrO₂ and CeO₂. This shows that V–O–Ti bonds play a key role in the oxidative dehydrogenation of ethyl lactate to ethyl pyruvate. In situ DRIFTS showed that the ethyl-propionate-2-oxide species on the catalyst surface are the key intermediates in this reaction via dehydrogenation. Molecular oxygen can replenish the surface oxygen, accelerating the oxidative dehydrogenation of ethyl lactate to ethyl lactate. This work allowed us to understand the chemical–physical features needed for a vanadium-oxide based catalyst to be active and selective in the ODH of ethyl lactate to ethyl pyruvate, thus opening new perspectives in the valorisation of bio-based platform molecules.

**Experimental section**

**Materials and instrumentation**

All chemicals were commercially available and used without further purification: anatase titania (Hombikat M311), (-)-ethyl L-lactate (Sigma–Aldrich, ≥98.0%, analytical standard), ammonium metavanadate (Acros Organics, 99.5%, analytical standard), oxalic acid (Sigma–Aldrich, ≥99.0%, analytical standard), vanadium(5+) oxide (Alfa Aesar, 99.2%), magnesium oxide nanopowder (Strem Chemicals, S.A. ≥ 230 m² g⁻¹, >95%), aluminium oxide (Sasol, S.A. = 181 m² g⁻¹, 97%), zirconium(IV) oxide nanopowder (Sigma–Aldrich, S.A. ≥ 25 m² g⁻¹, 99.0%), cerium(IV) oxide (Alfa Aesar, S.A. = 30–50 m² g⁻¹, 99.5%). X-ray diffraction patterns were recorded on a Rigaku Mini Flex II diffractometer using Cu-Kα radiation (λ = 1.5406 Å) at 35 kV and 30 mA. Nitrogen adsorption–desorption isotherms were measured using a Quantachrome Autosorb-3B instrument after evacuating the samples at 523 K for 6 h. The specific surface areas were evaluated using the Brunauer–Emmett–Teller method. The vanadium loading was measured by inductively coupled plasma (ICP) atomic emission spectroscopy (AES) using a Thermo IRIS Intrepid II XSP. UV-visible diffuse reflectance spectra were collected using a Jasco V670 spectrophotometer with Spectralon as a standard in the range 200–1000 nm. Scanning electron micrographs were recorded using a Hitachi S-4800 microscope. Temperature programmed reduction (TPR) measurements were performed using a 1100 Series Thermo Electron TPDRO machine by using a stream of 5% H₂/N₂ and a heating rate of 5 °C min⁻¹. XPS spectra were collected using a Thermo Scientific K-ALPHA with Al-K radiation (1486.6 eV), monochromatized by a twin crystal monochromator, yielding a
focused X-ray spot with a diameter of 400 μm, at 3 mA × 12 kV when charge compensation was achieved with the system flood gun that provides low energy electrons and low energy argon ions from a single source. The alpha hemispherical analyzer was operated in the constant energy mode with survey scan pass energies of 200 eV to measure the whole energy band and 50 eV in a narrow scan to selectively measure the particular elements. Estimation of the intensities was carried out after the calculation of each peak integral, S-shaped background subtraction and fitting the experimental curve to a combination of Lorentzian (30%) and Gaussian (70%) lines. Binding energies (BE), referenced to the C 1s line at 284.6 eV, have an accuracy of ±0.1 eV. In situ diffusion reflectance infrared Fourier transform (DRIFT) spectra were recorded using a Bruker Vertex 70 spectrometer equipped with a Pike DiffusIR cell attachment. The cell window was made of ZnSe. Spectra were recorded using a MCT detector after 128 scans at a 4 cm⁻¹ resolution. The instrument is online with an EcoSys-P mass spectrometer from European Spectrometry Systems. In each experiment, the sample was pretreated at 450 °C in He for 30 min in order to obtain a clean catalyst surface. Afterwards, the carrier gas was switched to air in the test in the presence of oxygen. Then the IR backgrounds were collected every 50 degrees from 450 °C to 50 °C. Afterwards, L-ethyl lactate (EL) pulsing was carried out at 50 °C. Then, the catalyst was kept under the carrier gas flow for 30 min in order to eliminate physisorbed molecules. The sample temperature was then increased at 5 °C min⁻¹ and spectra were collected every 50 °C. During the overall IR analysis, several mass signals (m/z) were monitored continuously: 4, 14, 15, 17, 18, 27, 28, 29, 31, 42, 43, 44, 45, 46, 58, 60, 61, 70, 74, 103, and 116. The conversion and selectivity were quantified using an Agilent 7820A GC equipped with a flame ionization detector (FID) and a dimethylpolysiloxane capillary column (VB-1, 30 m × 0.32 mm × 3.00 μm).

Preparation of V₂O₅/TiO₂

The supported vanadium oxide catalysts were prepared following the procedure reported by Srinivas et al. In a typical synthesis of V₂O₅/TiO₂ catalysts, TiO₂ was impregnated with aqueous solutions of ammonium metavanadate (NH₄VO₃) and oxalic acid, followed by drying and calcining for 4 h at 550 °C. The resulting solid was denoted as n-V₂O₅/TiO₂, where n represents the weight percent of V₂O₅ on TiO₂ (n = 1%, 3%, 5%, 10%, 20%).

Preparation of porous MgO, ZrO₂ and CeO₂

Porous MgO was prepared according to a previous report. 10 grams of magnesium hydroxide carbonate was calcined at 500 °C for 4 h at a heating rate of 1 °C min⁻¹ and then cooled to room temperature.

Porous ZrO₂ was prepared following the procedure reported by Davshan et al. 7.8 grams of cetyltrimethylammonium bromide (CTMABr) was added to 50 ml water. Then the pH value was adjusted to 2 by adding 2.0 M HCl solution. Next, zirconium propoxide solution (70 wt% in 1-propanol) was added to the premixed solution under rigorous stirring for 1 h. After that, the mixture was transferred into an autoclave and heated at 180 °C for 24 h. After that, the suspension was filtered, washed with water and dried at 80 °C overnight.

Procedure for catalytic experiments

The oxidative dehydrogenation of ethyl lactate to ethyl pyruvate was carried out in a fixed-bed quartz reactor with an internal diameter of 4 mm and a length of 300 mm. The catalyst (1 g, 20–25 mesh) was placed in the middle of the reactor and the upper part was filled with quartz sand for preheating the ethyl lactate. Ethyl lactate was injected into the reactor at a rate of 5 ml h⁻¹ using a syringe pump and using air as the carrier gas and terminal oxidant. After each reaction period of 2 h, the products were collected in a cold trap and a calculated amount of biphenyl was added as an external standard for GC analysis.

Conflicts of interest

There are no conflicts to declare.

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References