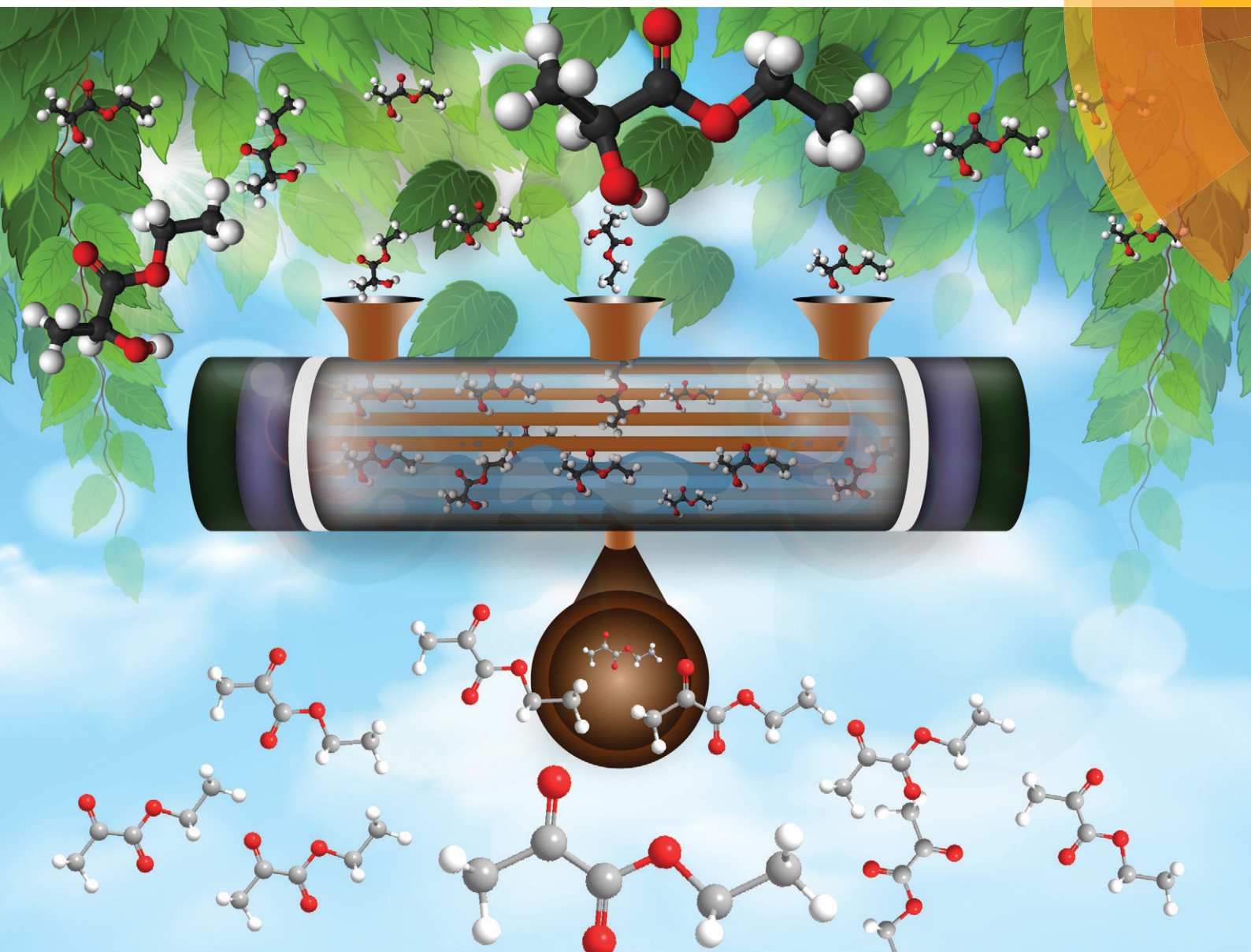


Catalysis Science & Technology

rsc.li/catalysis



ISSN 2044-4761



PAPER

N. Raveendran Shiju *et al.*

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

Expert reviewers.
Leading authors.
Discerning readers.
Committed editorial teams.

[View Article Online](#)
[View Journal](#) | [View Issue](#)

Our journals, books,
databases and literature
updating services are home
to world-class research.

That's down to the strength of our
international publishing community.

Together, we're advancing excellence
in the chemical sciences.

Browse the portfolio at
rsc.li/journals-impact

Registered charity number: 207890



PAPER



Cite this: DOI: 10.1039/c7cy02309j

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

Wei Zhang, ^a Giada Innocenti, ^{bc} Marilena Ferbinteanu, ^d Enrique V. Ramos-Fernandez, ^e Antonio Sepulveda-Escribano, ^e Haihong Wu, ^f Fabrizio Cavani, ^{bc} Gadi Rothenberg ^a and N. Raveendran Shiju ^{*,a}

We studied the vapour-phase oxidative dehydrogenation (ODH) of ethyl lactate with air to give ethyl pyruvate over V_2O_5/TiO_2 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 VO_x species was determined by XRD, UV-vis spectroscopy, XPS and H_2 -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 VO_x 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 V_2O_5/TiO_2 compared to vanadium supported on MgO, Al_2O_3 , ZrO_2 and CeO_2 . *In situ* DRIFT spectroscopy coupled with mass analysis shows that the reaction can involve three possible adsorption modes of ethyl lactate on the V_2O_5/TiO_2 surface. Under anaerobic conditions, 2-hydroxypropionate forms, giving ethyl acetate as the major product. Conversely, under aerobic conditions, oxygen that is chemisorbed on V_2O_5/TiO_2 is active and easily replenished from the gas phase, converting the ethyl-propionate-2-oxide intermediate into ethyl pyruvate.

Received 11th November 2017,
Accepted 19th February 2018

DOI: 10.1039/c7cy02309j

rsc.li/catalysis

Introduction

Lignocellulosic biomass is one of the few sources of truly renewable carbon.^{1,2} 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).^{3,4}

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.⁵ Today, pyruvates are still made *via* the classic dehydrative decarboxylation of tartaric acid in the presence of an excess of $KHSO_4$.^{6,7} 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.⁸ Several catalysts including Pd/Pt,⁹ iron phosphates,¹⁰ metal oxides (Mo, Ti, Zr, W and Sn),¹¹ and binary oxides (TeO_2-MoO_3 , SnO_2-MoO_3)^{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 CO_2 .⁵ 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.¹⁶ Compared with other oxide supports, titania interacts strongly with vanadia. The anatase phase in particular gives a stable VO_x monolayer with a catalytic oxidation

^a Van't Hoff Institute for Molecular Sciences, University of Amsterdam, P.O. Box 94157, 1090GD Amsterdam, The Netherlands.

E-mail: n.r.shiju@uva.nl; Web: <http://hims.uva.nl/hcsc>

^b Dipartimento di Chimica Industriale, ALMA MATER STUDIORUM Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

^c Consorzio INSTM, UdR di Bologna, Firenze, Italy

^d Faculty of Chemistry, Inorganic Chemistry Department, University of Bucharest, Dumbrava Rosie 23, Bucharest 020462, Romania

^e Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica-Instituto Universitario de Materiales, Universidad de Alicante, Ctra. San Vicente-Alicante s/n, E-03690 San Vicente del Raspeig, Spain

^f Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 North Zhongshan Road, Shanghai, 200062, China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7cy02309j

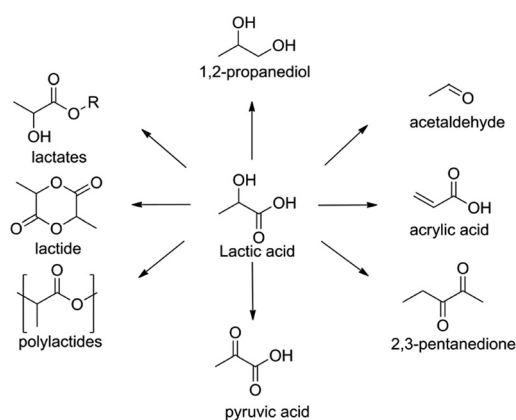
performance superior to that of rutile.^{17,18} We recently showed that TiO₂ itself can also catalyse the ODH of ethyl lactate to ethyl pyruvate in the liquid phase, due to its high affinity to ethyl lactate and oxygen.¹⁹ Meanwhile, Li *et al.* reported that MoVNbO_x supported on TiO₂ was more active than unsupported components for vapour phase ethyl lactate conversion.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.²¹ Our preliminary tests showed that commercial V₂O₅ gave higher yields of pyruvate compared with other oxides (MoO₃, TeO₂ and MoVO_x) at low temperatures (Fig. S1†). Thus, we hypothesised that VO_x/TiO₂ would be both active and selective in the ODH of lactates.

Here, we studied the structure–activity relationships in ethyl lactate ODH over V₂O₅/TiO₂ catalysts. We prepared a series of vanadium oxides supported on anatase titania, varying the vanadium loading *via* incipient wetness impregnation. Catalyst characterisation showed that different types of VO_x species (monomeric, polymeric, and crystalline domains) formed on the TiO₂ surface. We then examined the correlation between the VO_x structure and catalytic activity in the ODH of ethyl lactate with air in a fixed-bed reactor, comparing the catalytic properties of V₂O₅ impregnated on TiO₂, MgO, Al₂O₃, ZrO₂ and CeO₂. Across this series, V₂O₅/TiO₂ showed a superior ODH activity, which we attribute to the cooperative effects between vanadia and titania. *In situ* DRIFT spectroscopy showed that three adsorption modes of ethyl lactate are possible on the V₂O₅/TiO₂ surface. Under anaerobic conditions, 2-hydroxypropionate forms, giving ethyl acetate as the major product. Under aerobic conditions, oxygen chemisorbed on V₂O₅/TiO₂ 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_x/TiO₂ catalysts

First, we prepared five supported vanadium oxide catalysts by incipient wetness impregnation using aqueous solutions of



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

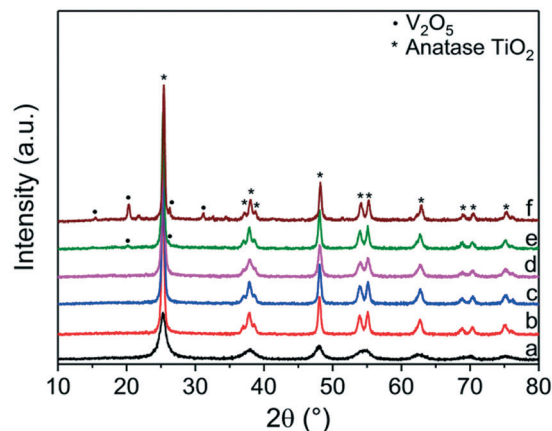


Fig. 1 X-ray diffraction patterns of VO_x/TiO₂ catalysts with different loadings of V₂O₅: (a) pristine TiO₂, (b) 1-V₂O₅/TiO₂, (c) 3-V₂O₅/TiO₂, (d) 5-V₂O₅/TiO₂, (e) 10-V₂O₅/TiO₂ and (f) 20-V₂O₅/TiO₂.

ammonium metavanadate (NH₄VO₃) and oxalic acid, which were subsequently dried and calcined at 550 °C. The samples are denoted as *n*-V₂O₅/TiO₂, where *n* represents the wt% of V₂O₅ on TiO₂ (*n* = 1%, 3%, 5%, 10%, 20%; see the Experimental section for details).

Fig. 1 shows the X-ray diffraction (XRD) patterns of the five catalysts. The crystalline structure of anatase TiO₂ remains stable after impregnation with vanadium oxide. No vanadia peaks are detected as the V₂O₅/(V₂O₅ + TiO₂) ratio increases from 1% to 5%. This suggests that amorphous vanadia species are well dispersed on the TiO₂ surface. When the V loading is increased to 10% and 20%, the peaks of crystalline V₂O₅ can be seen at 20.3° and 26.2°. This probably comes from polymeric vanadia species on the surface.²² Examining the surface morphology of VO_x/TiO₂ by scanning electron microscopy (SEM) upheld the XRD results (Fig. 2). All samples showed misshaped agglomerated granules and an increase in particle size with increasing vanadium content. The 20% loaded sample was hereafter discarded, because it contained essentially a separated V₂O₅ phase.

We then studied the textural properties of the catalysts using nitrogen adsorption–desorption isotherms. All samples

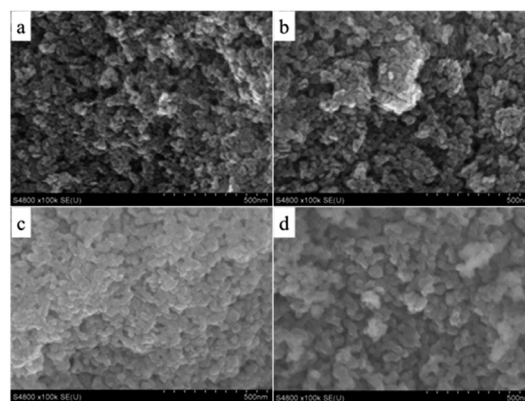


Fig. 2 Scanning electron micrographs of VO_x/TiO₂ catalysts: (a) 1-V₂O₅/TiO₂, (b) 3-V₂O₅/TiO₂, (c) 5-V₂O₅/TiO₂ and (d) 10-V₂O₅/TiO₂.

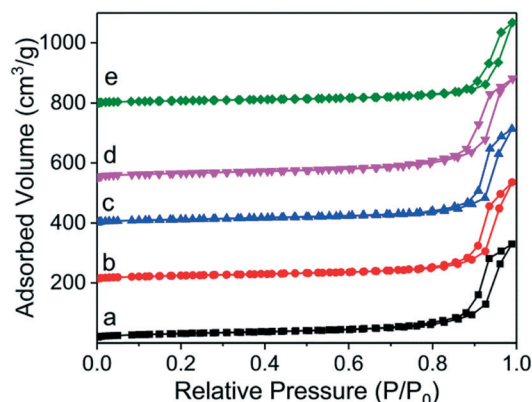


Fig. 3 Nitrogen adsorption-desorption isotherms of VO_x/TiO_2 catalysts. (a) Pristine TiO_2 , (b) $1\text{-V}_2\text{O}_5/\text{TiO}_2$, (c) $3\text{-V}_2\text{O}_5/\text{TiO}_2$, (d) $5\text{-V}_2\text{O}_5/\text{TiO}_2$ and (e) $10\text{-V}_2\text{O}_5/\text{TiO}_2$. The isotherms in the figure are shifted up for the sake of clarity.

Table 1 Textural properties of VO_x/TiO_2 catalysts

Sample	V content ^a (ICP, wt%)	V surface density (VO_x/nm^2)	S_{BET}^b ($\text{m}^2 \text{g}^{-1}$)	V_p^b ($\text{cm}^3 \text{g}^{-1}$)
Pure TiO_2	—	—	81.3	0.50
$1\text{-V}_2\text{O}_5/\text{TiO}_2$	0.58	0.8	81.2	0.52
$3\text{-V}_2\text{O}_5/\text{TiO}_2$	1.80	3.0	70.9	0.51
$5\text{-V}_2\text{O}_5/\text{TiO}_2$	2.70	4.8	66.3	0.49
$10\text{-V}_2\text{O}_5/\text{TiO}_2$	5.64	12.8	51.8	0.43

^a Determined by ICP analysis. ^b Calculated based on N_2 sorption at 77 K.

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 $81 \text{ m}^2 \text{g}^{-1}$ to $51 \text{ m}^2 \text{g}^{-1}$ (Table 1). Actually, the structure of surface VO_x species depends closely on the vanadium surface density ($\text{V}_{\text{atoms}} \text{nm}^{-2}$). The surface densities of our samples are 0.8, 3.0, 4.8 and $12.8 \text{ V}_{\text{atoms}} \text{nm}^{-2}$, corresponding to a V_2O_5 content of 1, 3, 5 and 10 wt%, respectively. The theoretic-

cal surface density value for monovanadate is $2\text{--}3 \text{ V}_{\text{atoms}} \text{nm}^{-2}$.¹⁵ Thus, the vanadia species of $1\text{-V}_2\text{O}_5/\text{TiO}_2$ and $3\text{-V}_2\text{O}_5/\text{TiO}_2$ are probably isolated VO_4 species, while $5\text{-V}_2\text{O}_5/\text{TiO}_2$ and $10\text{-V}_2\text{O}_5/\text{TiO}_2$ are predominantly polymeric VO_4 species and V_2O_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. $1\text{-V}_2\text{O}_5/\text{TiO}_2$ showed charge-transfer bands centred around $280\text{--}350 \text{ nm}$, which are assigned to isolated tetrahedral V^{5+} species.²⁵ As the V_2O_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 molybdenum²⁷). Increasing the vanadia content to 10 wt% showed crystalline V_2O_5 species (absorption at 490 nm ^{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 $[F(R_\infty)h\nu]^{1/2}$ vs. $h\nu$, where $F(R_\infty)$ is the Kubelka-Munk function and $h\nu$ is the incident photon energy.³¹ The corresponding E_g values for $\text{V}_2\text{O}_5/\text{TiO}_2$ are shown in Fig. 4B, wherein the value of pure TiO_2 is about 3.27 eV. For the $\text{V}_2\text{O}_5/\text{TiO}_2$ 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%, $E_g \approx 3.19 \text{ eV}$, which is close to the value of 3.21 eV for Na_3VO_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

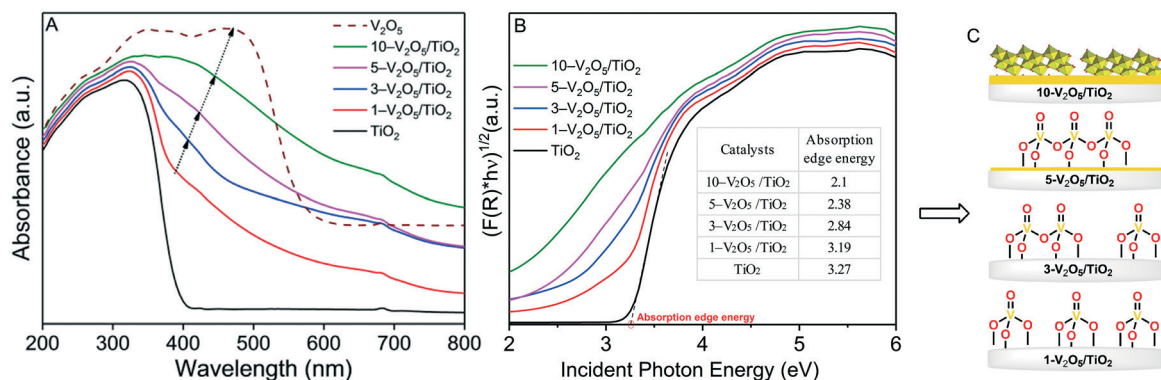


Fig. 4 (A) UV-vis absorption spectra of TiO_2 , V_2O_5 and $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts. (B) $[F(R_\infty)h\nu]^{1/2}$ plotted against the energy of the incident photon for the determination of edge energy for $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts; the inset shows the corresponding 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 $[F(R_\infty)h\nu]$. (C) Schematic structures of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts showing different types of vanadia species.

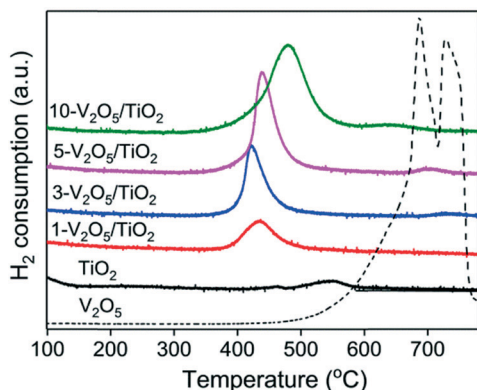


Fig. 5 H_2 -TPR profiles of the TiO_2 , V_2O_5 and $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts.

2.41 eV.³⁴ 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% $\text{V}_2\text{O}_5/\text{TiO}_2$ (2.10 eV) is close to that of bulk V_2O_5 (2.05 eV),¹⁵ 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 $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts (see Fig. 5).³⁵ 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 $\text{V}_2\text{O}_5/\text{TiO}_2$ is easier to reduce than pure TiO_2 or V_2O_5 . Among our $\text{V}_2\text{O}_5/\text{TiO}_2$ 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_x species in the monolayer are reported to be more easily reduced than monomeric ones.^{36,37} In our case, the 3- $\text{V}_2\text{O}_5/\text{TiO}_2$ sample, which also contains polymerized VO_4 units, was more easily reduced compared to the 1- $\text{V}_2\text{O}_5/\text{TiO}_2$ sample (which has only monomeric VO_4 species, in agreement with published data³⁸). 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- $\text{V}_2\text{O}_5/\text{TiO}_2$ and 10- $\text{V}_2\text{O}_5/\text{TiO}_2$ was even more difficult, in agreement with this trend.^{39,40}

We then ran X-ray photoelectron spectroscopy (XPS) measurements to identify the chemical species on the surface (see Fig. 6). The V 2 $p_{3/2}$ peak (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.¹⁷ The peaks at 464.7 eV and 458.9 eV are assigned to Ti 2 $p_{1/2}$ and Ti 2 $p_{3/2}$ (Fig. 6b), suggesting that the Ti^{4+} state predominates.⁴¹ 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_β). The peak at around 531.7 eV represented the surface chemisorbed oxygen (O_α), while that at 532.6 eV represented the chemisorbed water O'_α .^{34,42}

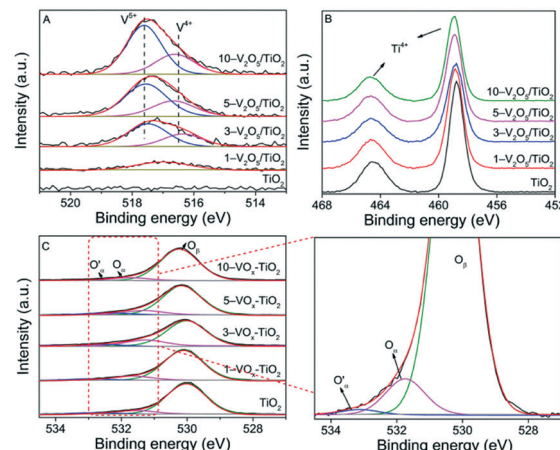


Fig. 6 XPS spectra of $\text{V}_2\text{O}_5/\text{TiO}_2$: (A) high resolution V_{2p} spectra, (B) high resolution Ti_{2p} spectra and (C) high resolution O_{1s} spectra.

Catalytic activity

We first analysed the mass-transfer limitations for the oxidative dehydrogenation of ethyl lactate with air over 3- $\text{V}_2\text{O}_5/\text{TiO}_2$ 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.⁴³

Then we studied the effect of reaction temperature on the ODH of ethyl lactate over 3- $\text{V}_2\text{O}_5/\text{TiO}_2$ (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.⁴⁴

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

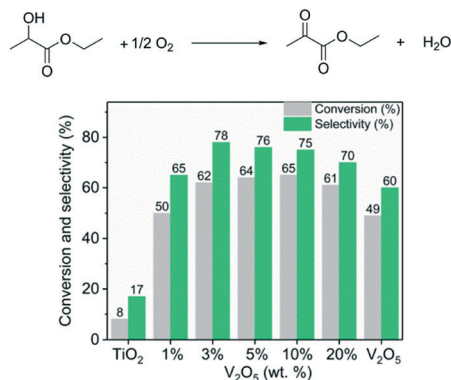


Fig. 7 The effect of V₂O₅ loading on ethyl lactate conversion and ethyl pyruvate selectivity over V₂O₅/TiO₂ catalysts. Reaction conditions: 5 ml h⁻¹ ethyl lactate, 2.25 L h⁻¹ air flow (molar ratio of ethyl lactate/O₂ = 2.3), 1.0 g catalyst, 200 °C.

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 TiO₂.⁴⁵

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 VO_x surface density increases, isolated VO₄ 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,⁴⁶ 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)];²⁴ 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 VO_x species is unrelated to the terminal V=O bonds in the partial oxidation of methanol.⁴⁷ 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

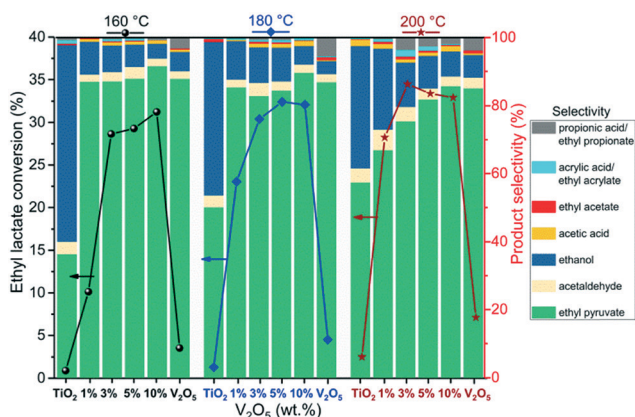


Fig. 8 The effect of V₂O₅ loading on ethyl lactate conversion and ethyl pyruvate selectivity over V₂O₅/TiO₂ catalysts. Reaction conditions: 8 ml h⁻¹ ethyl lactate, 1 L h⁻¹ air flow (molar ratio of ethyl lactate/O₂ = 8), 1.0 g catalyst, reaction temperature: 160 °C 180 °C and 200 °C.

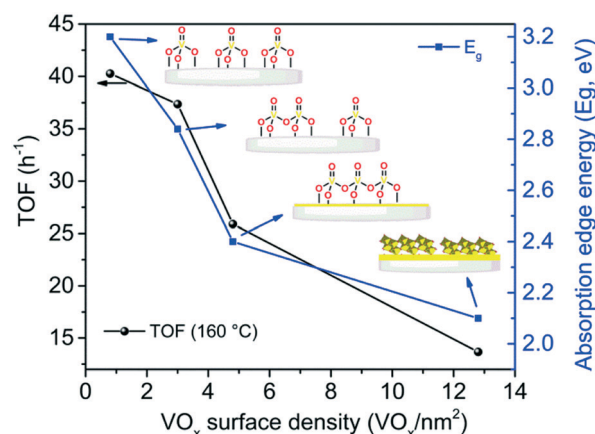


Fig. 9 Relationship between TOF of ethyl lactate oxidation, absorption edge energy (*E_g*) and VO_x surface density of VO_x/TiO₂ catalysts. Reaction conditions: 10 ml h⁻¹ ethyl lactate, 1 L h⁻¹ air flow (molar ratio of ethyl lactate/O₂ = 10), 1.0 g catalyst, 160 °C.

Table 2 ODH of ethyl lactate to ethyl pyruvate over V₂O₅ on various supports^a

Entry	Catalyst	S_{BET}^b (m ² g ⁻¹)	Con. ^c (%)	Sel. (%)	Yield ^c (%)	Surface pH ^d
1	1-V ₂ O ₅ /CeO ₂	50	1	32.2	Trace	6.75
2	1-V ₂ O ₅ /MgO	198	15.9	0.5	Trace	11
3	1-V ₂ O ₅ /ZrO ₂	89	28.5	43.9	12.5	5.9–6.1
4	1-V ₂ O ₅ /Al ₂ O ₃	278	35.6	36.7	13.1	8.9
5	1-V ₂ O ₅ /TiO ₂	81	58.7	63.7	37.4	6.0–6.4

^a Reaction conditions: 5 ml h⁻¹ ethyl lactate, 2.25 L h⁻¹ air flow (molar ratio of ethyl lactate/O₂ = 2.3), 1.0 g catalyst (1 wt% of metal oxide on TiO₂), 180 °C. ^b Calculated based on N₂ sorption at 77 K. ^c Determined by GC using biphenyl as an external standard. ^d Based on ref. 50 and 51.

does not play a role in our reaction.⁴⁷ For comparison, we prepared a mixture of V₂O₅ and TiO₂ by mixing bulk V₂O₅ and TiO₂ powder in a mortar. This physical mixture, which contained 3 wt% V₂O₅, gave only a yield of 5.6% ethyl pyruvate, compared to the 48.1% yield obtained over impregnated V₂O₅/TiO₂ (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 V–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: MgO, Al₂O₃, ZrO₂ and CeO₂, varying the support surface acidity.⁵⁰ For a fair comparison of V=O and V–O–V bonds, we prepared porous supports with a high surface area and subsequently impregnated 1 wt% of vanadium oxide on each support to form isolated 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 Al₂O₃ > TiO₂ > ZrO₂ > CeO₂ > MgO.^{53,54} In each case, we first tested the support alone in our reaction at 180 °C. Only MgO showed some conversion (13%) but no selectivity (because ethyl lactate undergoes hydrolysis to ethanol and lactic acid on the basic MgO surface). After introducing vanadia, the catalytic activities of the supported vanadia catalysts are summarized in Table 2. After impregnation, the reactivity of V₂O₅/MgO was unchanged. Conversely, the catalyst supported on acidic Al₂O₃ showed high conversion but low selectivity, owing to a competing decarboxylation of ethyl pyruvate to acetaldehyde.¹³ TiO₂-supported vanadium oxide showed the highest catalytic activity, while V₂O₅/ZrO₂ and V₂O₅/CeO₂ scarcely catalyzed the reaction under identical conditions. Fig. 10 shows the Arrhenius plots of ethyl lactate consumption rates. For 1-V₂O₅/TiO₂, the apparent activation energy (E_a) of ethyl lactate conversion (48 kJ mol⁻¹) is lower than that of 1-V₂O₅/Al₂O₃ (57 kJ mol⁻¹), 1-V₂O₅/ZrO₂ (75 kJ mol⁻¹) and 1-V₂O₅/CeO₂ (127 kJ mol⁻¹). These results confirmed that the monomeric V–O–Ti

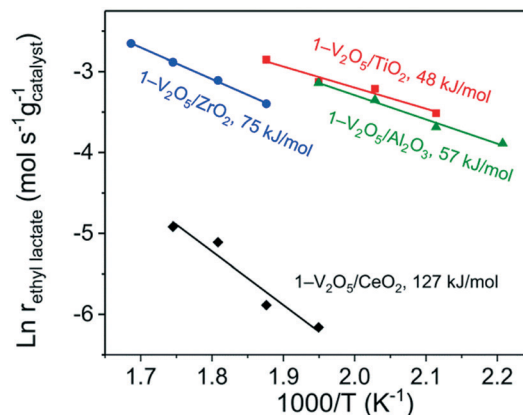


Fig. 10 Arrhenius plots for steady-state ethyl lactate conversion over supported V₂O₅ catalysts. Reaction conditions: LHSV = 4 h⁻¹, air flow = 1 L h⁻¹. Ethyl lactate consumption rate:

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

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

species is more catalytically active, confirming further the importance of the vanadium–oxygen interactions.

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-V₂O₅/TiO₂ in the absence of oxygen. The characteristic bands of ethyl lactate adsorbed on V₂O₅/TiO₂ 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 $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{s}}(\text{CH}_3)$, $\nu(\text{C–H})$, $\delta_{\text{as}}(\text{CH}_3)$, $\delta_{\text{s}}(\text{CH}_3)$ and $\delta(\text{C–H})$, respectively.^{55,56} These bands decreased in intensity with increasing temperature, indicating the degradation of ethyl lactate.⁵⁷ This process was also reflected by the changes of the carbonyl and carboxyl bands on the V₂O₅/TiO₂ surface (four peaks at 1730 cm⁻¹, 1667 cm⁻¹, 1566 cm⁻¹ and 1420 cm⁻¹, assigned to $\nu(\text{C=O})$, $\nu(\text{C=O}\cdots\text{M}^+)$, $\nu_{\text{s}}(\text{COO})$ and $\nu_{\text{as}}(\text{COO})$ vibrations, respectively).^{55,58,59} Increasing the temperature broadened these carbonyl and carboxyl peaks, and the signals of $\nu_{\text{s}}(\text{COO})$ and $\nu_{\text{as}}(\text{COO})$ 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 1651 cm⁻¹. These bands were assigned to the carbonyl stretching of the α -keto group of the pyruvate,⁵⁷ supporting the experimental results (Fig. S5†). The surface chemisorbed oxygen of V₂O₅/TiO₂ 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

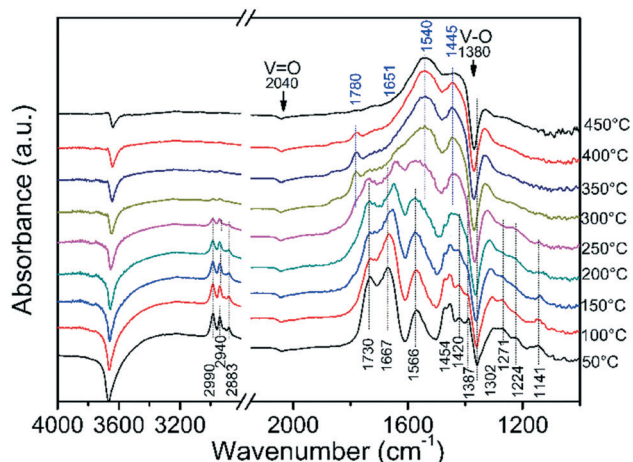


Fig. 11 *In situ* DRIFT spectra recorded during ethyl lactate temperature-programmed-desorption over 3-V₂O₅/TiO₂ with a He flow (without O₂).

(Table 3). 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,⁵⁵ 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 CO₂ 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-V₂O₅/TiO₂ with O₂. 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).

Upon increasing the temperature to 150 °C, we observed the characteristic bands of α -keto in pyruvate (1795 cm^{−1} and 1651 cm^{−1}),⁵⁷ together with a red-shifted COO stretch at 1597 cm^{−1}.^{55,62} The *in situ* DRIFTS also reflected the adsorption and dissociation of ethyl lactate on the V₂O₅/TiO₂ surface in the presence of oxygen. Due to the formation of pyruvate species, the position of carbonyl ν (C=O) was shifted to 1746 cm^{−1},⁶² as compared to the ν (C=O) of ethyl lactate at 1730 cm^{−1}; the peaks at 1141 cm^{−1} (C–O belongs to modes (a) and (b)) also started to weaken at 150 °C, accompanying the characteristic peaks of pyruvate, while the characteristic peaks of mode (c) were unchanged. This means that ethyl-propionate-2-oxide (in modes a and b) is the key intermediate to produce pyruvate (similar to the ethoxide species in ethanol oxidation^{60,61}). The decrease of the negative peak at 3662 cm^{−1} upheld this dehydration processes. Additionally, the intensity of pyruvate bands decreased as the temperature increased over 250 °C, indicating a decomposition process (Fig. S7†). The pyruvate peaks disappeared at 400 °C. Meanwhile, the new bands at 1520 cm^{−1} and 1445 cm^{−1} were attributed to surface carbonates ν_{as} (COO) and ν_s (COO),⁶³ as pyruvate is easily over-oxidised to form the carbonates as side products.⁶⁴

The bands at 2040 cm^{−1} and 1380 cm^{−1} are attributed to the V=O bond overtone band and the V–O bond combination band (probably belonging to V–O–Ti), respectively (for a detailed analysis of the pristine V₂O₅/TiO₂, see Fig. S8†).⁶¹ The presence of negative bands means that VO_x interacts with the adsorbed species. Under anaerobic conditions (Fig. 11), the V=O stretch remained constant with temperature, while V–O was blue-shifted (from 1360 cm^{−1} at 50 °C to 1380 cm^{−1} at 400 °C). In the presence of air, the V=O band is well preserved after the formation of the pyruvate band, and then vanishes at 350 °C along with pyruvate species; meanwhile, the V–O band, which diminished in intensity, is

Table 3 Ethyl lactate adsorption modes and their characteristic vibration wavenumber

<chem>CC(=O)OCH2CH3</chem> (a) <chem>CC(=O)OCH2CH3</chem> (b) <chem>CC(=O)OCH2CH3</chem> (c) <chem>CC(=O)OCH2CH3</chem> (d)			
Molecules	Vibrational mode	Wavenumber ^a (cm ^{−1})	Wavenumber ^b (cm ^{−1})
<chem>CC(=O)OCH2CH3</chem>	ν (C=O)	1725	1730
<chem>CC(=O)OCH2CH3</chem>	ν (C=O)	1668	1667
<chem>CC(=O)OCH2CH3</chem>	ν_s (COO)	1569	1566
<chem>CC(=O)OCH2CH3</chem>	ν_{as} (COO)	1450	1420
<chem>CC(=O)OCH2CH3</chem>	ν (C–O)	1058	Not detected
<chem>CC(=O)OCH2CH3</chem>	ν (C–O)	1118	Not detected
<chem>CC(=O)OCH2CH3</chem>	ν (C=O)	1614	Not detected

AL = Alcoholic functionalities. ^a Based on ref. 55 and 56. ^b From our *in situ* DRIFTS.

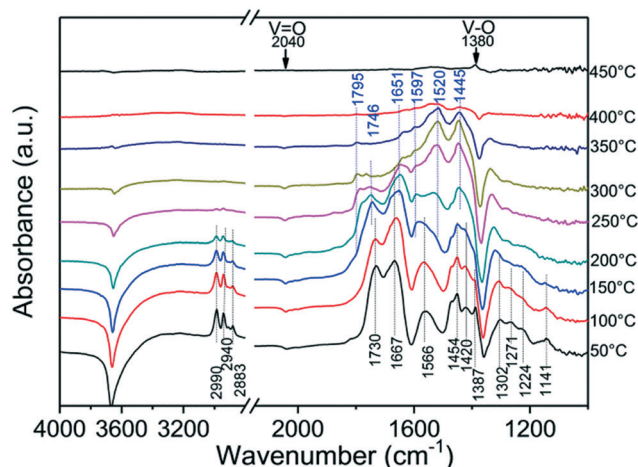


Fig. 12 *In situ* DRIFT spectra recorded during ethyl lactate temperature-programmed-desorption over 3- $\text{V}_2\text{O}_5/\text{TiO}_2$ with an air flow (with O_2).

still present at 400 °C in the presence of carbonates. These observations support the hypothesis that $\text{V}=\text{O}$ bonds are not involved in the ODH of ethyl lactate while $\text{V}-\text{O}$ 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 adsorbs and dissociates on the $\text{V}_2\text{O}_5/\text{TiO}_2$ 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.

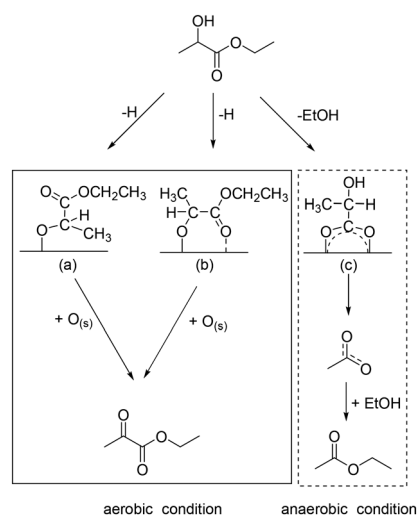


Fig. 13 Proposed reaction pathway for the aerobic and anaerobic conversion of ethyl lactate over $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts.

Conclusions

We studied the catalytic oxidative dehydrogenation of ethyl lactate to ethyl pyruvate over $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts. To explore the structure–activity relationship for various vanadia species, a series of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts with different surface densities were prepared *via* incipient wetness impregnation. As their surface density increases, the isolated VO_x species agglomerate into polymeric and crystalline VO_x species, leading to a decrease in TOF of ethyl lactate oxidation. The titania-supported vanadium oxide was superior to vanadia catalysts supported on MgO , Al_2O_3 , ZrO_2 and CeO_2 . This shows that $\text{V}-\text{O}-\text{Ti}$ 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 pyruvate. 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, $\geq 98.0\%$, analytical standard), ammonium metavanadate (Acros Organics, 99.5%, analytical standard), oxalic acid (Sigma-Aldrich, $\geq 99.0\%$, analytical standard), vanadium(v) oxide (Alfa Aesar, 99.2%), magnesium oxide nanopowder (Strem Chemicals, S.A. $\geq 230 \text{ m}^2 \text{ g}^{-1}$, $>95\%$), aluminium oxide (Sasol, S.A. $= 181 \text{ m}^2 \text{ g}^{-1}$, 97%), zirconium(iv) oxide nanopowder (Sigma-Aldrich, S.A. $\geq 25 \text{ m}^2 \text{ g}^{-1}$, 99.0%), cerium(iv) oxide (Alfa Aesar, S.A. $= 30\text{--}50 \text{ m}^2 \text{ g}^{-1}$, 99.5%). X-ray diffraction patterns were recorded on a Rigaku Mini Flex II diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) 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% H_2/N_2 and a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$. 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 $\times$ 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 $^{\circ}\text{C}$ 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 $^{\circ}\text{C}$ to 50 $^{\circ}\text{C}$. Afterwards, L-ethyl lactate (EL) pulsing was carried out at 50 $^{\circ}\text{C}$. 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 $^{\circ}\text{C min}^{-1}$ and spectra were collected every 50 $^{\circ}\text{C}$. 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 $\times$ 0.32 mm $\times$ 3.00 μm).

Preparation of $\text{V}_2\text{O}_5/\text{TiO}_2$

The supported vanadium oxide catalysts were prepared following the procedure reported by Srinivas *et al.*³³ In a typical synthesis of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts, TiO_2 was impregnated with aqueous solutions of ammonium metavanadate (NH_4VO_3) and oxalic acid, followed by drying and calcining for 4 h at 550 $^{\circ}\text{C}$. The resulting solid was denoted as $n\text{-V}_2\text{O}_5/\text{TiO}_2$, where n represents the weight percent of V_2O_5 on TiO_2 ($n = 1\%, 3\%, 5\%, 10\%, 20\%$).

Preparation of porous MgO , ZrO_2 and CeO_2

Porous MgO was prepared according to a previous report.⁶⁵ 10 grams of magnesium hydroxide carbonate was calcined at 500 $^{\circ}\text{C}$ for 4 hours at a heating rate of 1 $^{\circ}\text{C min}^{-1}$ and then cooled to room temperature.

Porous ZrO_2 was prepared following the procedure reported by Davshan *et al.*⁶⁶ 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 60 $^{\circ}\text{C}$ for 48 h. Then, the precipitate was filtered off and calcined at 600 $^{\circ}\text{C}$ for 2 h under an air flow.

Porous CeO_2 was synthesized according to the method described by Li *et al.*⁶⁷ Briefly, 5 grams of cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and 55 grams of NaOH were dissolved in 25 ml H_2O under vigorous stirring for 2 h. Then, the mixture was transferred into an autoclave and heated at 180 $^{\circ}\text{C}$ for 24 h. After that, the suspension was filtered, washed with water and dried at 80 $^{\circ}\text{C}$ 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 sands 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.

Acknowledgements

WZ thanks the China Scholarship Council for a PhD fellowship. EVRF thanks Generalitat Valenciana (project PROMETEOII/2014/004) and Ministerio de Economía y Competitividad (Spain) for projects MAT2013-45008-P, MAT2016-81732-ERC and RYC-2012-11427. This work is part of the Sustainable Chemistry Research Priority Area of the UvA (<http://suschem.uva.nl>).

References

- 1 A. Corma, S. Iborra and A. Vely, *Chem. Rev.*, 2007, **107**, 2411.
- 2 P. N. R. Vennestrom, C. M. Osmundsen, C. H. Christensen and E. Taarning, *Angew. Chem., Int. Ed.*, 2011, **50**, 10502.
- 3 M. Dusselier, P. Van Wouwe, A. Dewaele, E. Makshina and B. F. Sels, *Energy Environ. Sci.*, 2013, **6**, 1415.
- 4 R. Beerthuis, G. Rothenberg and N. R. Shiju, *Green Chem.*, 2015, **17**, 1341.
- 5 P. Mäki-Arvela, I. L. Simakova, T. Salmi and D. Y. Murzin, *Chem. Rev.*, 2014, **114**, 1909.
- 6 E. Erlenmeyer, *Ber. Dtsch. Chem. Ges.*, 1881, **14**, 320.
- 7 F. Howard, *Org. Synth.*, 1941, **1**, 475.
- 8 F. A. Castillo Martinez, E. M. Balciunas, J. M. Salgado, J. M. Domínguez González, A. Converti and R. P. d. S. Oliveira, *Trends Food Sci. Technol.*, 2013, **30**, 70.

- 9 S. Sugiyama, T. Kikumoto, H. Tanaka, K. Nakagawa, K.-I. Sotowa, K. Maehara, Y. Himeno and W. Ninomiya, *Catal. Lett.*, 2009, **131**, 129.
- 10 M. Ai and K. Ohdan, *J. Mol. Catal. A: Chem.*, 2000, **159**, 19.
- 11 S. Sugiyama, N. Shigemoto, N. Masaoka, S. Suetoh, H. Kawami, K. Miyaoura and H. Hayashi, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 1542.
- 12 H. Hayashi, S. Sugiyama, N. Masaoka and N. Shigemoto, *Ind. Eng. Chem. Res.*, 1995, **34**, 135.
- 13 S. Lomate, T. Bonnotte, S. Paul, F. Dumeignil and B. Katryniok, *J. Mol. Catal. A: Chem.*, 2013, **377**, 123.
- 14 I. E. Wachs and B. M. Weckhuysen, *Appl. Catal., A*, 1997, **157**, 67.
- 15 A. Khodakov, B. Olthof, A. T. Bell and E. Iglesia, *J. Catal.*, 1999, **181**, 205.
- 16 C. A. Carrero, R. Schloegl, I. E. Wachs and R. Schomaecker, *ACS Catal.*, 2014, **4**, 3357.
- 17 Q. Shi, Y. Li, E. Zhan, N. Ta and W. Shen, *CrystEngComm*, 2015, **17**, 3376.
- 18 M. Inomata, K. Mori, A. Miyamoto, T. Ui and Y. Murakami, *J. Phys. Chem.*, 1983, **87**, 754.
- 19 E. V. Ramos-Fernandez, N. J. Geels, N. R. Shiju and G. Rothenberg, *Green Chem.*, 2014, **16**, 3358.
- 20 X. Zhao, C. Zhang, C. Xu, H. Li, H. Huang, L. Song and X. Li, *Chem. Eng. J.*, 2016, **296**, 217.
- 21 A. Chieragato, J. M. López Nieto and F. Cavani, *Coord. Chem. Rev.*, 2015, **301–302**, 3.
- 22 D. W. Kwon, S. M. Lee, J. M. Won and S. C. Hong, *J. Chem. Eng. Jpn.*, 2015, **48**, 463.
- 23 F. Cavani, E. Foresti, F. Trifiró and G. Busca, *J. Catal.*, 1987, **106**, 251.
- 24 P. Ji, X. Gao, X. Du, C. Zheng, Z. Luo and K. Cen, *Catal. Sci. Technol.*, 2016, **6**, 1187.
- 25 F. Blanco-Bonilla, S. Lopez-Pedrajas, D. Luna, J. M. Marinas and F. M. Bautista, *J. Mol. Catal. A: Chem.*, 2016, **416**, 105.
- 26 F. M. Bautista, J. M. Campelo, D. Luna, J. Luque and J. M. Marinas, *Appl. Catal., A*, 2007, **325**, 336.
- 27 C. Caro, K. Thirunavukkarasu, M. Anilkumar, N. R. Shiju and G. Rothenberg, *Adv. Synth. Catal.*, 2012, **354**, 1327.
- 28 K. V. Bineesh, D.-K. Kim, M.-I. L. Kim and D.-W. Park, *Appl. Clay Sci.*, 2011, **53**, 204.
- 29 D. Nitsche and C. Hess, *J. Phys. Chem. C*, 2016, **120**, 1025.
- 30 H. Tian, E. I. Ross and I. E. Wachs, *J. Phys. Chem. B*, 2006, **110**, 9593.
- 31 X. Gao and I. E. Wachs, *J. Phys. Chem. B*, 2000, **104**, 1261.
- 32 E. V. Danilevich, G. Y. Popova, T. V. Andrushkevich, V. V. Kaichev, I. G. Danilova, Y. A. Chesalov, V. A. Rogov, V. I. Bukhtiyarov and V. N. Parmon, *Appl. Catal., A*, 2014, **475**, 98.
- 33 D. Srinivas, W. F. Hölderich, S. Kujath, M. H. Valkenberg, T. Raja, L. Saikia, R. Hinze and V. Ramaswamy, *J. Catal.*, 2008, **259**, 165.
- 34 D. W. Kwon, K. H. Park and S. C. Hong, *Appl. Catal., A*, 2015, **499**, 1.
- 35 J. Beckers and G. Rothenberg, *Dalton Trans.*, 2008, 6573.
- 36 P. Concepción, M. T. Navarro, T. Blasco, J. M. López Nieto, B. Panzacchi and F. Rey, *Catal. Today*, 2004, **96**, 179.
- 37 M. V. Martínez-Huerta, X. Gao, H. Tian, I. E. Wachs, J. L. G. Fierro and M. A. Bañares, *Catal. Today*, 2006, **118**, 279.
- 38 Z. Li, K. Su, B. Cheng, D. Shen and Y. Zhou, *Catal. Lett.*, 2010, **135**, 135.
- 39 B. Schimmoeller, H. Schulz, A. Ritter, A. Reitzmann, B. Kraushaar-Czametzk, A. Baiker and S. E. Pratsinis, *J. Catal.*, 2008, **256**, 74.
- 40 D. W. Kwon, S. M. Lee and S. C. Hong, *Appl. Catal., A*, 2015, **505**, 557.
- 41 K. Sivaranjani, A. Verma and C. S. Gopinath, *Green Chem.*, 2012, **14**, 461.
- 42 H. Zhao, S. Bennici, J. Shen and A. Auroux, *Appl. Catal., A*, 2009, **356**, 121.
- 43 A. P. Amrute, C. Mondelli, M. Moser, G. Novell-Leruth, N. López, D. Rosenthal, R. Farra, M. E. Schuster, D. Teschner, T. Schmidt and J. Pérez-Ramírez, *J. Catal.*, 2012, **286**, 287.
- 44 J. Zhang, Y. Zhao, M. Pan, X. Feng, W. Ji and C.-T. Au, *ACS Catal.*, 2010, **1**, 32.
- 45 M. Gallastegi-Villa, A. Aranzabal, Z. Boukha, J. A. González-Marcos, J. R. González-Velasco, M. V. Martínez-Huerta and M. A. Bañares, *Catal. Today*, 2015, **254**, 2.
- 46 Q. Wang and R. J. Madix, *Surf. Sci.*, 2002, **496**, 51.
- 47 G. Deo and I. E. Wachs, *J. Catal.*, 1994, **146**, 323.
- 48 I. E. Wachs and B. M. Weckhuysen, *Appl. Catal., A*, 1997, **157**, 67.
- 49 I. E. Wachs, J.-M. Jehng, G. Deo, B. M. Weckhuysen, V. V. Gulians and J. B. Benziger, *Catal. Today*, 1996, **32**, 47.
- 50 I. E. Wachs, *Dalton Trans.*, 2013, **42**, 11762.
- 51 T. Blasco and J. M. L. Nieto, *Appl. Catal., A*, 1997, **157**, 117.
- 52 I. E. Wachs, J.-M. Jehng, G. Deo, B. M. Weckhuysen, V. V. Gulians, J. B. Benziger and S. Sundaresan, *J. Catal.*, 1997, **170**, 75.
- 53 J. Datka, A. M. Turek, J. M. Jehng and I. E. Wachs, *J. Catal.*, 1992, **135**, 186.
- 54 S. Velu, M. P. Kapoor, S. Inagaki and K. Suzuki, *Appl. Catal., A*, 2003, **245**, 317.
- 55 Y.-K. Chen, Y.-F. Lin, Z.-W. Peng and J.-L. Lin, *J. Phys. Chem. C*, 2010, **114**, 17720.
- 56 G. Cassanas, M. Morssli, E. Fabrégue and L. Bardet, *J. Raman Spectrosc.*, 1991, **22**, 409.
- 57 B. Wen, Y. Li, C. Chen, W. Ma and J. Zhao, *Chem. – Eur. J.*, 2010, **16**, 11859.
- 58 K. Krauß, A. Drochner, M. Fehlings, J. Kunert and H. Vogel, *J. Mol. Catal. A: Chem.*, 2000, **162**, 413.
- 59 A. Chieragato, C. Bandinelli, P. Concepción, M. D. Soriano, F. Puzzo, F. Basile, F. Cavani and J. M. L. Nieto, *ChemSusChem*, 2017, **10**, 234.
- 60 V. V. Kaichev, Y. A. Chesalov, A. A. Saraev, A. Y. Klyushin, A. Knop-Gericke, T. V. Andrushkevich and V. I. Bukhtiyarov, *J. Catal.*, 2016, **338**, 82.
- 61 F. Folco, J. Velasquez Ochoa, F. Cavani, L. Ott and M. Janssen, *Catal. Sci. Technol.*, 2017, **7**, 200.
- 62 K. Hanai, A. Kuwae, K.-K. Kunitomo and S.-I. Kitoh, *Eur. J. Chem.*, 2014, **5**, 305.
- 63 O. Seifert, K. Wolter, B. Dillmann, G. Klivenyi, H. J. Freund, D. Scarano and A. Zecchina, *Surf. Sci.*, 1999, **421**, 176.

- 64 S. C. A. Sousa and A. C. Fernandes, *Coord. Chem. Rev.*, 2015, **284**, 67.
- 65 Y.-D. Ding, G. Song, X. Zhu, R. Chen and Q. Liao, *RSC Adv.*, 2015, **5**, 30929.
- 66 N. A. Davshan, A. L. Kustov, O. P. Tkachenko, L. M. Kustov and C. H. Kim, *ChemCatChem*, 2014, **6**, 1990.
- 67 J. Li, Z. Zhang, Z. Tian, X. Zhou, Z. Zheng, Y. Ma and Y. Qu, *J. Mater. Chem. A*, 2014, **2**, 16459.