



Selective Air Oxidation of Biobased Lactate to Pyruvate Catalyzed by Abundant-Element Heterogeneous Catalysts

W. Zhang

Summary

The current chemical industry relies heavily on nonrenewable fossil carbon sources, resulting in the emission of greenhouse gases and other environmental problems. Moreover, the finite fossil reserves cannot sustain the rapid growth of demand for ever. Developing renewable sources has become an urgent task and a driving force for the evolution of the modern chemical industry.

Biomass, the most abundant renewable carbon source, is considered as a 'green' alternative to fossil carbon sources. There is a growing interest in upgrading of biomass into commodity chemicals, primarily through a set of simple building blocks, so-called 'platform molecules'. Lactic acid and its esters are among such promising biomass-derived platform molecules. They can be converted into a variety of important industrial chemicals, including acrylic acid, lactide, acetaldehyde, pyruvates, 1,2-propanediol and 2,3-pentanedione. In particular, pyruvate esters are important chemicals used in many sectors, such as agrochemicals, foodstuffs, cosmetics, and pharmaceuticals. As pyruvate is a key metabolite, it can be biologically produced from sugars in microorganisms. However, the main drawback of metabolic process is its low productivity and costly purification of pyruvate. Today, most of pyruvates are still made via the eco-unfriendly pyrolysis of tartaric acid with stoichiometric KHSO_4 as a dehydrating agent.

Alternatively, the catalytic oxidative dehydrogenation of lactates with molecular oxygen is a promising route for producing pyruvates. This route is more sustainable than the current industrial standard, ideally giving water as the only byproduct. But there are not many literature reports on it, as the direct aerobic oxidation of lactate to pyruvate is a challenging process. On one hand, molecular oxygen is the most abundant and the cheapest oxidant but has a high activation barrier. Its activation requires noble metal catalysts or harsh reaction conditions. On the other hand, once dioxygen is activated, the oxygen-rich pyruvate product is easily over-oxidized to unwanted products. As such, the aim of this work is to develop abundant-element heterogeneous catalysts with high activity, selectivity and stability for air oxidation of lactates to pyruvates.

Chapter 1 introduced the concept of sustainable chemistry, listing a set of criteria, principles and metrics of green chemistry to help us address challenges in climate change, nature resource scarcity and environment pollution. An overview on the biomass valorization to renewable chemicals is then given, especially on catalytic upgrading of lactic acid/lactates to commodity chemicals.

Chapter 2 started by screening various metal oxides supported on activated

carbon for the air oxidation of ethyl lactate to ethyl pyruvate in liquid phase. Vanadium-based catalyst can efficiently catalyse this reaction under mild conditions. Many studies show that doping carbon materials with nitrogen atoms can facilitate catalytic oxidation reactions, but how does it happen? We then study the effects of various nitrogen-containing additives in our reaction system, aiming to understand the effect of such additives on the aerobic oxidation of lactates (**Figure 1**). We found that vanadia species acts synergistically with homogeneous pyridine-type additives, giving high conversion and selectivity. Control experiments and DFT calculations 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 designed 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.

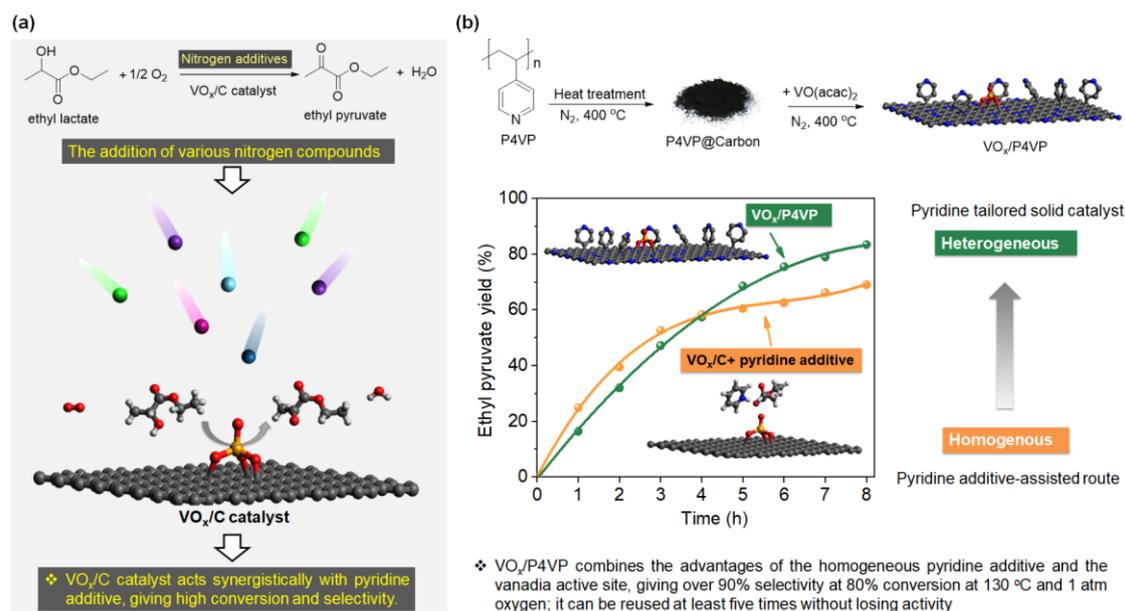


Figure 1. Graphical summary of the results from Chapter 2. (a) The influence of nitrogen additives on the oxidation of ethyl lactate in the presence of VO_x/C catalyst; (b) schematic illustration of the synthesis of $\text{VO}_x/\text{P4VP}$ catalyst, and comparisons of ethyl pyruvate yield over $\text{VO}_x/\text{P4VP}$ and $\{\text{VO}_x/\text{C} + \text{pyridine}\}$ catalysts.

Based on the findings described in Chapter 2, we hypothesized that integrating the vanadia sites into nitrogen-doped carbon structures could lead to efficient heterogeneous catalysts for the selective oxidation of lactate to pyruvate. **Chapter 3** presents a simple synthetic strategy for preparing nitrogen-doped carbon nanosheets (NCNs) starting from two abundant precursors, melamine and glucose, and using a simple thermal-annealing process (**Figure 2**). The resulting NCNs feature numerous edges and holes for anchoring vanadium oxides (V-NCNs). This creates cooperative catalytic sites that boost the catalytic oxidation of ethyl lactate to ethyl pyruvate. Additionally, we systematically studied the surface nitrogen species of NCNs by varying the pyrolysis temperature, and found that the active pyridinic N-oxide species, formed in a high thermal-annealing treatment, acts synergistically with vanadium active sites in converting ethyl lactate with oxygen into ethyl pyruvate under mild conditions. Our V-NCNs catalyst is among the best non-noble metal heterogeneous catalysts for the liquid-phase aerobic oxidation of lactate to pyruvate.

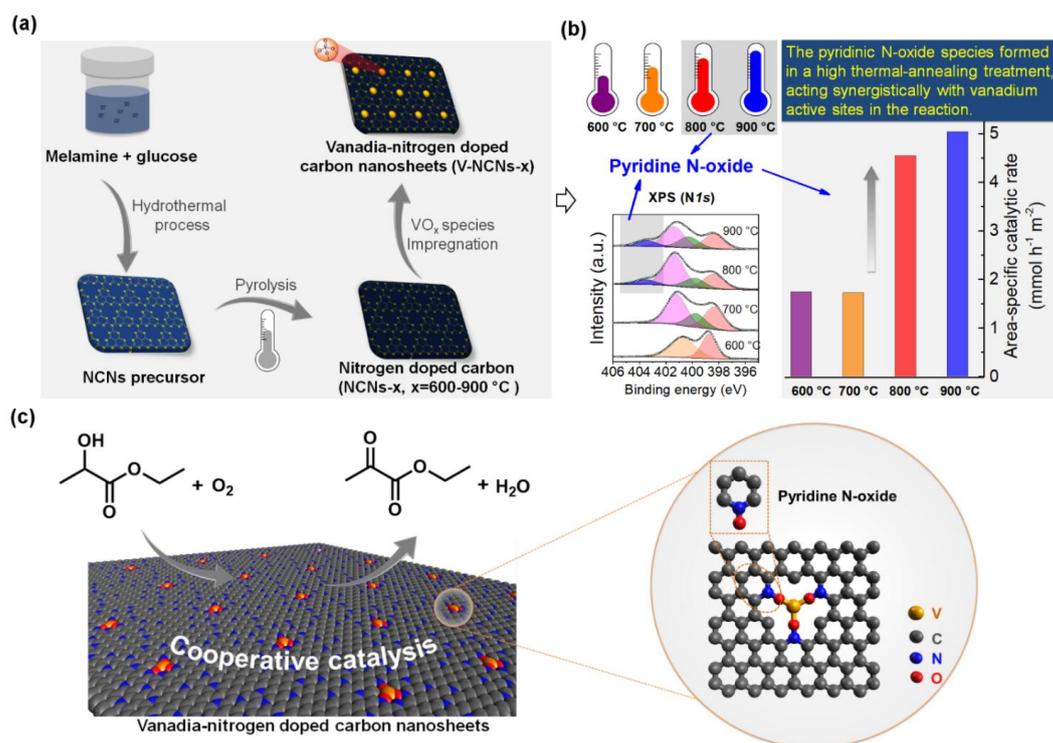


Figure 2. Graphical summary of the results from **Chapter 3**. (a) Schematic illustration of the synthesis route to nitrogen-doped carbon nanosheet supports (NCNs) and their combination with vanadium oxide to give V-NCNs. (b) XPS spectra of N 1s in the V-NCNs-x (x=600-900 °C) (left) and plots of area-specific conversion rate of ethyl lactate against the pyrolysis temperature (right). (c) Schematic representation of synergistic effect of pyridinic N-oxide species in this reaction over V-NCNs catalyst.

Running the aerobic oxidation of lactates in vapor-phase is more economic and effective than in liquid-phase, but also less selective. **Chapter 4** describes the vapour-phase oxidative dehydrogenation of ethyl lactate with air to give ethyl pyruvate over V_2O_5/TiO_2 catalysts in a fixed-bed reactor. A series of V_2O_5/TiO_2 with different surface densities were prepared via incipient wetness impregnation (**Figure 3**). 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, which can be easily replenished from the gas phase, converting the ethyl-propionate-2-oxide intermediate to ethyl pyruvate.

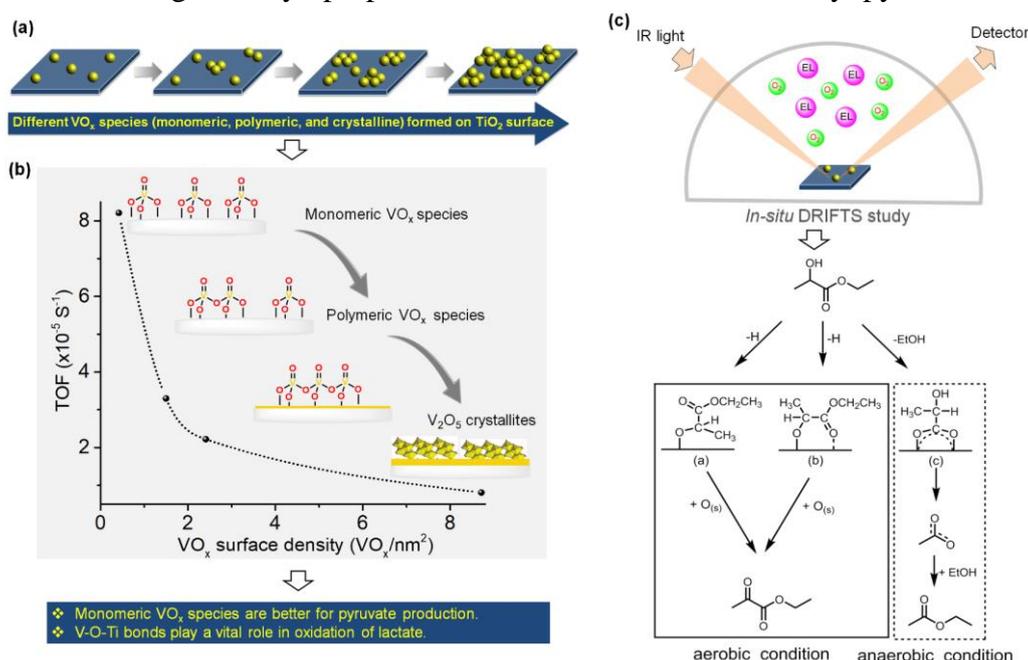


Figure 3. Graphical summary of the results from Chapter 4. (a) Schematic description of vanadium oxides supported on titania support (VO_x/TiO_2) varying the vanadium loading via incipient wetness impregnation (b) Relationship between turnover frequency (TOF) of ethyl lactate oxidation and VO_x surface density of VO_x/TiO_2 catalysts (c) Schematic of *in situ* DRIFT study of ethyl lactate temperature-programmed-desorption over $3-VO_x/TiO_2$ with air, and proposed three adsorption modes of ethyl lactate on the catalyst surface.

As discussed in the Chapter 4 and above, highly dispersed vanadia on anatase TiO_2 are desired for an efficient oxidation. However, the density of isolated vanadyl species is limited by the titania surface area, and distributing the sites evenly on the surface is problematic at high loadings. **Chapter 5** reports a one-pot synthesis method for mesoporous vanadia-titania (VTN), acting as a highly efficient and recyclable catalysts for the conversion of ethyl lactate to ethyl pyruvate (**Figure 4**). These VTN materials feature high surface areas, large pore volumes and high density of isolated vanadium species, which can expose the active sites and facilitate the mass transport. Compared to homogeneous vanadium complexes and VO_x/TiO_2 prepared by impregnation, the meso-VTN catalysts showed superior activity, selectivity and stability in the aerobic oxidation of ethyl lactate to ethyl pyruvate. V^{4+} as the major valence state was incorporated into the lattice of NH_4VO_3 derived VTN material, yielding more $\text{V}^{4+}\text{-O-Ti}$ bonds in anatase-dominant structure. *In situ* DRIFT spectroscopy and density functional theory calculations show that $\text{V}^{4+}\text{-O-Ti}$ bonds are responsible for the dissociation of ethyl lactate over VTN catalysts, and for further activating the deprotonation of β -hydrogen. Molecular oxygen can replenish the surface oxygen to regenerate the $\text{V}^{4+}\text{-O-Ti}$ bonds.

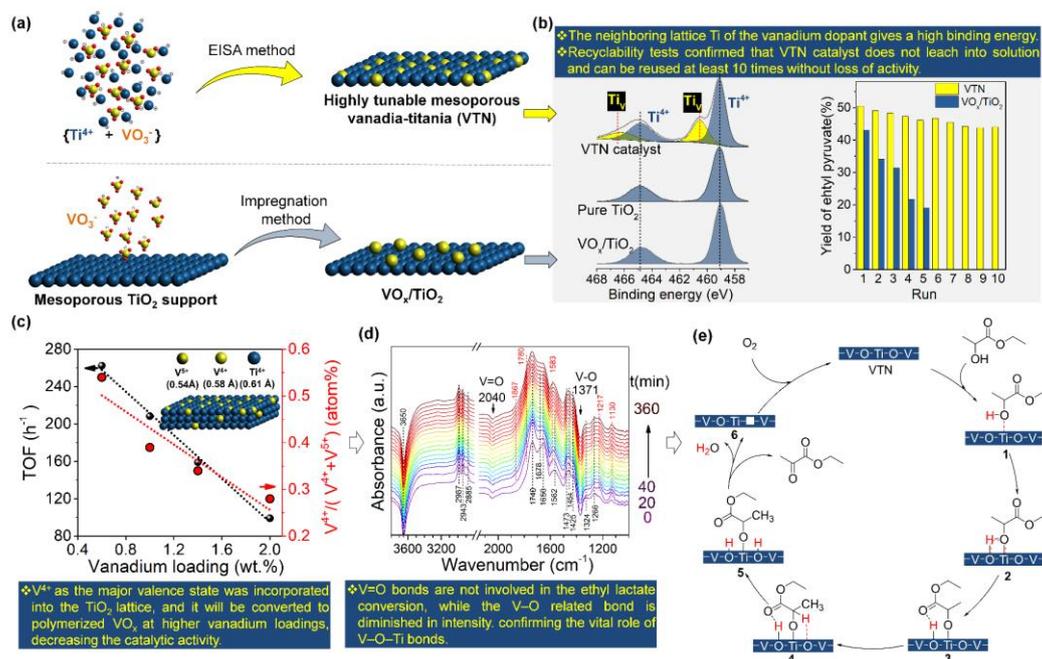


Figure 4. Graphical summary of the results from Chapter 5. (a) Schematic illustration of the synthesis route of mesoporous vanadia-titania (VTN), compared to the VO_x/TiO_2 via incipient wetness impregnation. (b) XPS studies showing that the substitution of lattice Ti by vanadium in VTN catalyst (left), and recycling of VTN and VO_x/TiO_2 in the oxidation of ethyl lactate to ethyl pyruvate in liquid phase. (c) Relationship between turnover frequency (TOF) for ethyl pyruvate formation, $\text{V}^{4+}/(\text{V}^{4+}+\text{V}^{5+})$ (atom %) and vanadium loading catalysts. (d) *In situ* DRIFT spectra recorded during aerobic oxidation of ethyl lactate with air over VTN at different time intervals. (e) Proposed mechanism of lactate-to-pyruvate reaction over VTN catalyst.

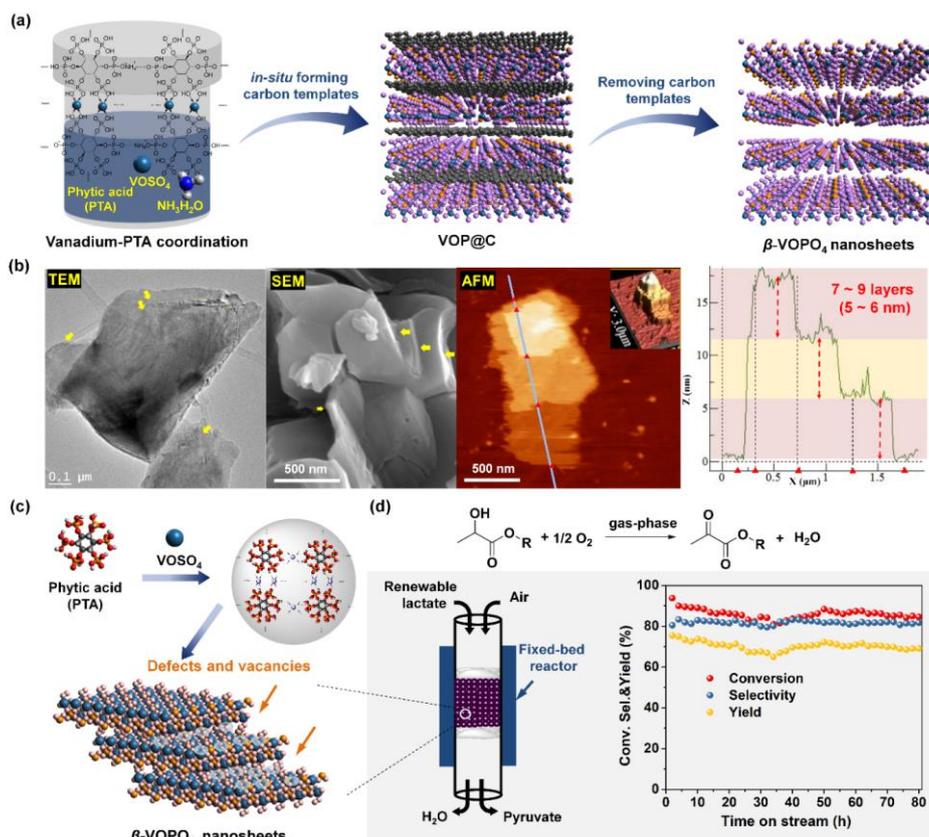


Figure 5. Graphical summary of the results from Chapter 6. (a) Schematic illustration of the synthesis procedure for 2D β -VOPO₄ nanosheets. (b) Morphological and microstructural characterization of β -VOPO₄ nanosheets confirmed by TEM, SEM and AFM analysis. (c) Schematic representation of phytic acid-derived VOPO₄ nanosheets with abundant defects and vacancies. (d) Schematic illustration of vapour-phase oxidative dehydrogenation of ethyl lactate with air to give ethyl pyruvate in a fixed-bed reactor over β -VOPO₄ nanosheets, and its stability test at optimized conditions (WHSV=3 h⁻¹, T=300 °C).

Vanadium phosphorus oxide (VPO) are comprised of alternating vanadium octahedra (VO₆) and phosphate tetrahedra (PO₄), in which the orthorhombic β phase is the most thermodynamically stable phase. However, β -VOPO₄ has rarely been used in catalysis. In **Chapter 6** we report a new template-free and scalable method for preparing two-dimensional (2D) β -VOPO₄ ultrathin nanosheets with controllable layers (**Figure 5**). The key to this synthesis is using cheap vanadyl sulphate (VOSO₄) and phytic acid (PTA) precursors. The synthesis method is facile and scalable via a two-step process (hydrothermal and calcination treatment). Our nanosheets are industrially viable catalysts cost wise as well. PTA acts as a strong chelating agent, but can also be carbonized *in situ* into carbon templates, which are responsible for the precisely controlled few-layer nanosheets. The resulting 2D β -VOPO₄ ultrathin nanosheets expose abundant V⁴⁺/V⁵⁺ redox sites and oxygen vacancies, leading to an

efficient oxidation catalyst. We demonstrate the high catalytic activity of this material in the vapour-phase aerobic oxidation of ethyl lactate to ethyl pyruvate. Importantly, this β -VOPO₄ does not get hydrated, thereby reducing the competing hydrolysis reaction by water by-product. These nanosheets show superior selectivity compared to analogous vanadyl phosphates. They are also highly stable, maintaining a steady-state conversion of ~ 90% (with >80% selectivity) for at least 80 h on stream without losing their activity.

In conclusion, we have developed a series of new abundant-element heterogeneous catalysts for selective air oxidation of lactate to pyruvate in liquid phase and in vapour phase. For this, we tried to follow a holistic approach which the synthesis methods are designed to give catalysts with well-defined structures characterized by multiple, complementary techniques, catalytic activity evaluation and kinetic analysis, operando spectroscopies, and DFT calculations. This work provides fundamental insights for developing further simple and cost-effective catalytic systems for highly efficient conversion of biomass derivatives to value-added chemicals under mild conditions.