Selective Aerobic Oxidation of Lactate to Pyruvate Catalyzed by Vanadium-Nitrogen-Doped Carbon Nanosheets

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Supporting Information

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Experimental Section

Materials and instrumentation

All chemicals were obtained from commercial sources and used without further purification: Melamine (Sigma-Aldrich, 99%), D–(+)-Glucose (Sigma-Aldrich, ≥ 99.95%), Pluronic® F-127, vanadyl acetylacetonate (VO(acac)_2, Sigma-Aldrich, 98%), (−)-Ethyl L-lactate (Sigma-Aldrich, ≥ 98.0%), diethyl succinate (Sigma-Aldrich, 99%).

X-ray diffraction patterns (XRD) were recorded on a Rigaku Mini Flex II diffractometer instrument using Cu–Kα radiation (λ = 1.5406 Å) at 35 kV and 30 mA. Transmission electron microscopy (TEM) were carried out using a JEOL-JEM-2100F microscope, equipped with a field emission gun (FEG) and an ultra-high resolution pole-piece that provided a point-to-point resolution of 0.19 nm (TEM and STEM samples were dispersed in ethanol, sonicated and sprayed on a carbon-coated copper grids and then allowed to air-dry). Nitrogen sorption isotherms were measured on a Quantachrome Autosorb–3B instrument after evacuating the samples at 423 K for 5 h. The specific surface areas were evaluated using the Brunauer–Emmett–Teller method and the pore distribution was calculated by BJH method. The vanadium loading was measured by inductively coupled plasma atom emission spectroscopy (ICP-AES) on a Thermo IRIS Intrepid II XSP. The ex-situ X-ray photoelectron spectroscopy (XPS) measurements were performed on a SPECS spectrometer equipped with a Phoibos 100 MCD analyzer and a monochromatized X-ray Al Kα. High resolution spectra were taken with an energy pass of 30 eV and an energy step of 0.1 eV. An estimation of the intensities was done after a calculation of
each peak integral, S-shaped background subtraction and fitting the experimental curve to a combination of a 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. Gas chromatography (GC) analysis was collected by an Agilent 7820A instrument equipped with a flame ionization detector (FID), autosampler (G4513A) and a dimethylpolysiloxane capillary column (VB-1, 30 m × 0.32 mm × 3.00 μm).

Procedure for nitrogen-doped holey-carbon nanosheets (NCNs-x) preparation

For a typical synthesis procedure of NCNs-800, melamine (6 mmol, 0.75 g) and glucose (12 mmol, 2.16 g) were ultrasonically dispersed in 40 mL aqueous Pluronic® F-127 (2 g) solution for 2 h. Then, the mixture was transferred to Teflon autoclave, heating at 180 °C for 12 h in an oven. Next, the resulting suspension was cooled to room temperature, the solid was filtered and washed with water and acetone three times, subsequent drying in a vacuum oven at 80 °C overnight to obtained NCNs precursor. The resulting NCNs precursor was loaded into a tube furnace, and heated to 800 °C for 4 h with a heating rate of 2 °C/min in the flowing Argon. The obtained black solid was NCNs-800 nanosheets. According to the above similar procedure, the NCNs-x samples were synthesized respectively by annealing at different temperatures (x represents the pyrolysis temperature, x=600, 700, 800 and 900 °C).

Procedure for NCNs-x supported vanadium oxide (V-NCNs-x) preparation

The V-NCNs-800 catalyst was prepared according to a previous report.[1] 1 grams of the resulting NCNs-x sample was dispersed into 50 mL ethanolic solution. Then, vanadyl acetylacetonate (VO(acac)₂, 87 mg) was added to the mixture by stirring at 80 °C overnight to remove the ethanol solvent. After that, the solid was ground by mortar and pestle to fine powder, followed by a calcination treatment at 400 °C for 4 h under nitrogen, with a heating rate of 2 °C/min in a nitrogen flow. The resulting black powder was denoted as V-NCNs-800. The catalysts V-NCNs-600, V-NCNs-700, V-NCNs-900 similarly prepared from the respective precursors (NCNs-x).

Procedure for mesoporous carbon nitride supported vanadium oxide (V-mpg-C₃N₄) preparation

Mesoporous carbon nitride was prepared following the procedure reported by Thomas et al.[2] 2 grams of cyanamide was added into LUDOX® HS-40 colloidal silica aqueous solution (40 wt.%) by stirring for 2 h at 70 °C to form transparent solution. Then, the mixture was heated at 100 °C until removal water. The resultant solid was ground and then loaded into a tube furnace, heating to 550 °C for 4 h at a rate of 2.3 °C/min in the flowing Argon. The obtained yellow powder was then added into NH₄HF₂ solution (4M) for two days to remove the silica template. After filtering, the precipitate was washed with water and acetone three times, and dry at 80 °C overnight to obtained mpg-C₃N₄. Next, 1 grams of resultant mpg-C₃N₄ was impregnated with ethanolic solution of vanadyl acetylacetonate (VO(acac)₂, 87
mg), followed by drying and calcining for 4 h at 400 °C in Ar flow. The resulting solid was denoted as V-mpg-C₃N₄.

**Procedure for catalyst testing**

In a typical reaction, ethyl lactate (5 mmol), catalyst (25 mg), molecular sieve-3 Å (dehydrating agent, 100 mg) and diethyl succinate (1 ml, solvent) were added in a 25 ml flask equipped with a dioxygen balloon. The reaction mixture was heated to 130 °C under magnetic stirring (800 rpm). After reaction, the flask was cooled to room temperature. Next, the product was filtered using 0.45 µm PTFE syringe filters. Then, the filtrate was diluted with acetone and then analyzed by gas chromatography. The catalyst was filtered, washed with water and acetone for several times, and then dried at 80 °C in vacuum for the next cycle. The conversion of ethyl lactate (EL) and selectivity of ethyl pyruvate (EP) were calculated by the following formulas:

\[
EL \text{ conversion (mol%)} = \frac{n_{EL}^0 - n_{EL}}{n_{EL}^0} \times 100 \% \tag{1}
\]

\[
EP \text{ selectivity (mol%)} = \frac{n_{EP}}{n_{EL}^0 - n_{EL}} \times 100 \% \tag{2}
\]

\[
EP \text{ yield (mol%)} = \frac{n_{EP}}{n_{EL}^0} \times 100 \% \tag{3}
\]

where \(n_{EL}^0, n_{EL}\) and \(n_{EP}\) were related to the initial mole content of EL, the final mole content of EL, and the mole content of produced EP, respectively.

The turnover frequency (TOF) and the area-specific conversion rate of ethyl lactate (\(r_{EL}\)) were calculated by the following equations:

\[
TOF(\text{h}^{-1}) = \frac{n_{EL}^0 - n_{EL}}{n_{Vanadium} \times t(\text{h})} \tag{4}
\]

\[
r_{EL}(\text{mmol} \cdot \text{h}^{-1} \cdot \text{m}^{-2}) = \frac{n_{EL}^0 - n_{EL}}{S_{\text{Catal}} \times m_{\text{catal}} \times t(\text{h})} \tag{5}
\]

where the \(n_{Vanadium}\) is the vanadium mole content of V-NCNs-\(x\) catalyst. \(S_{\text{Catal}}\) is the surface area of the catalyst (m²/g), \(m_{\text{catal}}\) is catalyst amount (g), and \(t(\text{h})\) is the reaction time. Note: we studied the TOFs and \(r_{EL}\) at low conversions (<15%).
**Figure S1** FT-IR spectra of graphitic carbon nitride (g-C₃N₄), NCNs precursor and V-NCNs-x catalysts.

**Figure S2** Representative high-resolution HRTEM images of pure carbon nanosheets (CNs).
**Table S1** Textural properties of the V-NCNs-x samples.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m(^2)/g) (^a)</th>
<th>( V_{\text{total}} ) (cm(^3)/g) (^a)</th>
<th>Average pore diameter (nm) (^b)</th>
<th>C (wt.%) (^c)</th>
<th>N (wt.%) (^c)</th>
<th>V loading (wt.%) (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>V-NCNs-600</td>
<td>100.6</td>
<td>0.47</td>
<td>13</td>
<td>84.2</td>
<td>4.1</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>V-NCNs-700</td>
<td>124.7</td>
<td>0.46</td>
<td>14</td>
<td>86.8</td>
<td>3.0</td>
<td>1.2</td>
</tr>
<tr>
<td>3</td>
<td>V-NCNs-800</td>
<td>129.9</td>
<td>0.54</td>
<td>45</td>
<td>88.7</td>
<td>2.9</td>
<td>1.2 (1.0 (^e))</td>
</tr>
<tr>
<td>4</td>
<td>V-NCNs-900</td>
<td>133.6</td>
<td>0.56</td>
<td>48</td>
<td>90.1</td>
<td>2.9</td>
<td>1.1</td>
</tr>
</tbody>
</table>

\(^a\) Calculated (based on N\(_2\) sorption at 77 K). \(^b\) Calculated from BJH method. \(^c\) Determined by elemental analysis. \(^d\) Determined by ICP analysis. \(^e\) vanadium loading of the V-NCNs-800 after using 5 times.

**Figure S3** X-ray diffraction patterns of V-NCNs-x catalysts, where x represents the pyrolysis temperature, x=600, 700, 800 and 900 °C.
Figure S4 High-resolution V2p spectra of the V-NCNs-x catalysts (x= 600, 700, 800 and 900). The two additional small peaks in the V-NCNs-900 sample can be attributed to the V(0), probably originating from the reduction of a small amount of vanadium species at high pyrolysis temperature.
**Figure S5** Recycling of 3-V-NCNs-800 catalyst in the aerobic oxidation of ethyl lactate to ethyl pyruvate. Reaction conditions: ethyl lactate 5 mmol, catalyst 25 mg, 1 atm O$_2$, diethyl succinate (solvent, 1 ml), molecular sieve-3 Å (dehydrating agent, 100 mg), 130 °C and 9 h.

**Figure S6** TEM images of the V-NCNs-800 after using 5 times.
**Figure S7** Raman spectra of fresh V-NCNs-800 and after using in the reaction for 5 times, in comparison to activated carbon supported vanadium oxide (VO\textsubscript{x}/AC).

**References**
