High-Performance Vapor-Phase Selective Oxidation of Ethyl Lactate to Ethyl Pyruvate over SiO$_2$ Supported PMoVNb Oxides

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Abstract: This paper describes the application of P-Mo-V-Nb/SiO$_2$ catalysts for the selective oxidation of ethyl lactate (EL) to ethyl pyruvate (EP). The P-Mo-V-Nb/SiO$_2$ catalysts exhibit superior performance for EP selectivity than the corresponding samples of binary V-Nb/SiO$_2$, ternary P-Mo-V/SiO$_2$ and P-Mo-Nb/SiO$_2$ catalysts at same temperatures. The origin of high EP selectivity of the P-Mo-V-Nb/SiO$_2$ catalysts is explored and attributed to the synergistic effect of P, Mo, V, and Nb mixed oxides presented on the surface of the catalyst. The highly dispersive sites separated active species under the action of phosphorus, suppressing over oxidation and improving the selectivity. The existence of MoO$_3$ to provide higher oxidation for catalyst. The redox cycle of V and Nb oxides could be completed through electron transfer between lattice oxygen and metal cations. Moreover, the weak acidity of catalyst surface is favorable to avoid the decarboxylation reaction to target a high selectivity of EP. Therefore, the P-Mo-V-Nb/SiO$_2$ catalyst obtained the maximum yield of 91.8% with a selectivity of 93.8% and a conversion of 99.0% simultaneously at 280 °C.

Keywords: biomass conversion; selective oxidation; PMoVNb; ethyl lactate; ethyl pyruvate

1. Introduction

In recent years, biomass has attracted increasing interest due to rising fossil fuel prices and global warming [1]. Conversion of biomass-based platform compounds to prepare valuable chemicals is a promising utilization approach. Lactic acid is an important compound which has been commercially produced by the fermentation of biomass. Lactic acid, its esters, and salts are feed for many downstream products such as pyruvate.

Pyruvate and its esters are important chemicals widely used in food, spice, cosmetics, pharmaceutical and other industries [2–4]. Currently, pyruvate and its esters are still produced mainly via the energy-intensive pyrolysis of tartaric acid with KHSO$_4$ as a dehydrating agent [5,6]. Unfortunately, this process obtains a yield of only 50–54% but obviously negative environmental effect due to the use of numerous dehydrating agents. Pyruvic chemicals can also be produced through enzymatic conversion or glucose fermentation [7–9]. However, these approaches are difficult to industrialize due to critical conditions including reaction temperature and acidity. Lactic acid and its esters can be selectively oxidized to pyruvates and corresponding esters. This is a green and atom-economical reaction route which has received extensive attention from the scientific and
industrial circles. This highly atom-efficient catalytic oxidative dehydrogenation process includes liquid and vapor phase strategies [5,10–14].

The liquid-phase process employs various metal oxides as catalysts at a low temperature. FeO₃, TiO₂, V₂O₅/MgO-Al₂O₃, ZrO₂, CeO₂, and ZnO were demonstrated alternative catalysts, in which TiO₂ was the most efficient [15]. Zhang et al. reported a one-pot synthesis of mesoporous vanadia-titania, acting as an efficient and recyclable catalyst for the conversion of ethyl lactate (EL) to ethyl pyruvate (EP) [16]. This reaction was carried out with molecular oxygen at 130 °C for 8 h. The selectivity of EP decreased from 91% to 58% when the conversion of EL increased from 20% to 70% with the reaction time on stream. Lu et al. discovered a more efficient catalyst under mild conditions. Tremendously, 100% EL conversion and 97.8% EP yield were obtained after reaction at 50 °C for 9 h [17]. However, the use of H₂O₂ aqueous solution (molar ratio of H₂O₂ to EL 2.80) reduces likelihood of industrialized application because of the expense of H₂O₂ and the explosive risk of peroxides. Moreover, a low reaction temperature was demanded strictly because higher reaction temperature (70 °C) lead to fast hydrolysis and decarboxylation of EP. In addition, the space time yield is usually not high in liquid-phase process, and the recycle of catalysts is strenuous.

In contrast, selective oxidation is more likely industrialized in vapor phase, which is advantage in continuous operation, process control and space time yield. Several vapor-phase catalysts have been studied and disclosed for the selective oxidation of EL to EP. Sugiyama’s research team [10] reported a series of bimetallic catalysts containing MoO₃, SnO₂-MoO₃, FeO₃-MoO₃, and Te-MoO₃, where SnO₂-MoO₃ obtained the highest yield of 36% at 250 °C. They proposed the collaborative participation of lattice and gas-phase oxygen according the XPS results. Thereafter, Zhao et al. [18] employed Mo0.61V0.31Nb0.08Ox/TiO2 as a catalyst to obtain a yield of 47% at 170 °C. They discovered that oxygen concentration was the only factor affecting the reaction rate rather than the concentration of ethyl lactate on the surface. This apparent first-order reaction is consistent with the Mars–van Krevelen redox mechanism.

However, the application is limited due to the low activity and selectivity. The separation of EL and EP is energy intensive, because the difference of their boiling point is only 1 K. Other byproducts from decarboxylation added the energy consumption of separation. It remains a great challenge to develop a highly effective and selective catalyst.

MoVOₓ-based composite oxides exhibits excellent catalytic activity and selectivity in the oxidation of light alkanes at relatively low temperatures [19–21]. Mo-V-P-Oₓ/Al₂O₃ and Mo-V-Te-Nb-O composite oxides catalysts [22,23] are efficient in the ammonidation of propane to acrylonitrile. MoVNbOₓ show high catalytic performance for the oxidation of ethane [24], ethylene [25], and ethanol [26]. Despite synergistic effect in multi-component oxides is still indistinct, multiple oxides may be inexpensive and selective catalysts for the selective oxidation. To the best of our knowledge, there is no report about the oxidative dehydrogenation of EL to EP over P-Mo-V-Nb catalysts.

Here we report a P-Mo-V-Nb catalyst supported on SiO₂ for the selective oxidation of ethyl lactate to ethyl pyruvate. This quaternary component oxide was compared with binary V-Nb and ternary P-Mo-V and P-Mo-Nb catalysts prepared with an equal volume impregnation method. The resulting catalysts were systematically characterized by nitrogen adsorption, XRF, XRD, H₂-TPR, XPS, NH₃-TPD, pyridine FT-IR and Raman and evaluated in a fixed bed to understand the effect of the molybdenum and vanadium species of structure and redox properties.

2. Results and Discussion

2.1. Structural Properties

The elemental analysis results of all samples by XRF are shown in Table 1. The molar ratio of P/Si, Mo/Si, V/Si, and Nb/Si remained almost unchanged from that of the experimental design (0.89, 0.74, 0.16, and 0.02). The equal volume impregnation method used is efficient to introduce binary V-Nb, ternary P-Mo-V, P-Mo-Nb, and quaternary P-Mo-V-Nb mixed oxide into silica.
Table 1. Molar ratio of P/Si, Mo/Si, V/Si, and Nb/Si by XRF

<table>
<thead>
<tr>
<th>Samples</th>
<th>P/Si</th>
<th>Mo/Si</th>
<th>V/Si</th>
<th>Nb/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V-Nb/SiO2</td>
<td>-</td>
<td>-</td>
<td>0.17</td>
<td>0.02</td>
</tr>
<tr>
<td>P-Mo-Nb/SiO2</td>
<td>0.91</td>
<td>0.75</td>
<td>0.18</td>
<td>-</td>
</tr>
<tr>
<td>P-Mo-V/SiO2</td>
<td>0.89</td>
<td>0.73</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>P-Mo-V-Nb/SiO2</td>
<td>0.88</td>
<td>0.74</td>
<td>0.15</td>
<td>0.03</td>
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</tbody>
</table>

The N₂ adsorption-desorption isotherms and the textural properties of catalyst samples are given in Figure 1 and Table 1. The SiO₂ and V-Nb/SiO₂ samples exhibit type II adsorption isotherm patterns, which display no adsorption saturation at relatively higher pressure with H₃-type hysteresis loops, indicating the existence of the large mesoporous channel structure. The P-Mo-V/SiO₂, P-Mo-Nb/SiO₂, and P-Mo-V-Nb/SiO₂ samples have H₄ hysteresis loops which adsorption branch is a composite of type I and type II isotherms patterns, suggesting the channel structure with micropores and mesopores [27,28]. Table 1 lists the detailed mesoporous sizes of the sample, which are consistent with the N₂ adsorption isotherm analysis. From the pore-size distribution curves (Figure 1B) of these samples, it could be seen that the nanopore size of silica was a bit large with a peak value at 11nm. The V-Nb/SiO₂ had a wide distribution range at 5–40nm. Meanwhile, the nanopore size of P-Mo-V /SiO₂, P-Mo-Nb/SiO₂, and P-Mo-V-Nb/SiO₂ in Figure 1B were dominantly distributed in the range of 1-4nm, and the peak values respectively at 1.8nm, 2.0nm and 1.5nm. In addition, it could be obviously observed that the samples showed smaller pore sizes and smaller Brunauer–Emmett–Teller (BET) surface areas with increasing the amount of active species. The BET surface areas of the four catalysts ranged 127 to 9.7m²/g with the pore volume of 1.2 to 0.1cm³/g smaller than those (208.76m²/g and 1.2cm³/g) of the supported silica (Table 2). This could demonstrate that the active species was well dispersed in the surface of the support as well as in the channels.

Figure 1. (A) N₂ adsorption-desorption isomers of samples: SiO₂, V-Nb/SiO₂, P-Mo-V/SiO₂, P-Mo-Nb/SiO₂ and P-Mo-V-Nb/SiO₂; and (B) Barrett–Joyner–Halenda (BJH) measurements of SiO₂, V-Nb/SiO₂, P-Mo-V/SiO₂, P-Mo-Nb/SiO₂, and P-Mo-V-Nb/SiO₂.
Table 2. Textural parameters of the samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>(S_{\text{BET}}) (m(^2)/g) (^a)</th>
<th>(V_p) (cm(^3)/g) (^a)</th>
<th>(D_p) (nm) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>208</td>
<td>1.2</td>
<td>11.6</td>
</tr>
<tr>
<td>V-Nb/SiO(_2)</td>
<td>127</td>
<td>1.2</td>
<td>18.3</td>
</tr>
<tr>
<td>P-Mo-Nb/SiO(_2)</td>
<td>17.2</td>
<td>0.2</td>
<td>18.3</td>
</tr>
<tr>
<td>P-Mo-V/SiO(_2)</td>
<td>9.1</td>
<td>0.1</td>
<td>17.1</td>
</tr>
<tr>
<td>P-Mo-V-Nb/SiO(_2)</td>
<td>9.7</td>
<td>0.1</td>
<td>15.1</td>
</tr>
</tbody>
</table>

\(^a\) \(S_{\text{BET}}\): Brunauer–Emmett–Teller (BET) surface area; \(D_p\): pore diameter; \(V_p\): volume.

Figure 2 gives diffraction patterns obtained with different catalysts. Only two crystallites V\(_2\)O\(_5\) and Nb\(_2\)O\(_5\) were observed in Figure 1b, and the other catalysts showed a large peak at 23.8\(^o\) like carrier silica but the diffraction intensity was weaker than it. The diffraction disappeared for P-Mo-Nb/SiO\(_2\), P-Mo-V/SiO\(_2\), and P-Mo-V-Nb/SiO\(_2\) catalysts, indicating the high dispersion of active component on the surface of the carrier silica. Considering the three catalysts have a common P species different from V-Nb/SiO\(_2\), the above results could attributed to the fact that P species can make the other active species dispersed on the surface of the carrier better.

The Raman spectra of all catalyst samples are shown in Figure 3. No typical Raman peaks of silica was detected, but the right side of the baseline shift to higher may be caused by the fluorescence of the silica. For the V-Nb/SiO\(_2\), the band at 1019cm\(^{-1}\) is assigned to V=O stretches in monovanadates and polyvanadates, and the bands at 998, 690, 516, and 268cm\(^{-1}\) are assigned to crystallized V\(_2\)O\(_5\) [29,30]. The P-Mo-V/SiO\(_2\), P-Mo-Nb/SiO\(_2\), and P-Mo-V-Nb/SiO\(_2\) show the intense band at 964, 880, and 395cm\(^{-1}\), corresponding to crystallized MoO\(_3\). Besides, the broad band at 1052–1294 cm\(^{-1}\) is assigned to M=O terminal stretches [31,32]. For P-Mo-V/SiO\(_2\) and P-Mo-V-Nb/SiO\(_2\), in Figure 3, the bands at 1025cm\(^{-1}\) is implied to mixed Mo-O-V phases. Because of P having a lone pair of electrons, it could tend the electron to the Mo site or V site and increased the negative charge of oxygen on Mo=O or V=O, which made the redox process easier [33]. For P-Mo-Nb/SiO\(_2\) and
P-Mo-V-Nb/SiO₂, the band near 920 cm⁻¹ is characteristic of Mo₅O₁₄-type structure [34], this would be consistent with the promotion of such structure upon niobium doping [35].

![Raman spectra](image)

**Figure 3.** Raman spectra of (a–e): SiO₂, V-Nb/SiO₂, P-Mo-V/SiO₂, P-Mo-Nb/SiO₂, and P-Mo-V-Nb/SiO₂.

### 2.2. Redox Properties

The reducibility of the samples was studied by H₂-temperature-programmed reduction (TPR) (Figure 4). The position of the reduction peak represents the ease of catalyst reduction, and the lower the peak temperature, the easier it is to reduce, that is, the stronger redox ability. The peak area was the amount of H₂ consumption by the reduction of the catalyst, representing the total amount of species that can be reduced. From the Figure 4a, the carrier silica has a very weak redox peak, and the V-Nb/SiO₂ is observed a single peak near 440–748 °C, which is assigned to reduction of V⁵⁺ to V³⁺ in polyvanadates. The P-Mo-V/SiO₂, P-Mo-Nb/SiO₂, and P-Mo-V-Nb/SiO₂ could be observed two reduction peaks obviously. The first H₂ consumption peak (Figure 4c,e) at the range of 356–706 °C, which could be assigned to the overlapped reduction peaks of Mo⁶⁺ and V⁵⁺ in Mo-O-V structures to Mo⁴⁺ and V³⁺ respectively[35,36]. It could be assigned to reduction of Mo⁶⁺ to Mo⁵⁺ in Figure 4d. Compared to the V-Nb/SiO₂, the redox ability of P-Mo-V/SiO₂, P-Mo-Nb/SiO₂, and P-Mo-V-Nb/SiO₂ is improved as T_max shifting to lower values. The addition of P and Mo improves the mobility of oxygen species, so that the transfer of lattice oxygen can be performed at a lower temperature. The two types of reduction peaks Mo⁶⁺ to Mo⁴⁺ and V⁵⁺ to V³⁺ could explain this phenomenon [36,37]. Besides, the addition of P promotes the active species dispersed as well as make the redox process easier [37,38]. The peak ranged at 650–900 °C undergo three stages upon reduction: (a) strongly dispersed monomeric octahedral coordinated Mo and polymolybdates Mo⁶⁺→Mo⁵⁺ (600–750 °C); (b) MoO₃ crystal and tetrahedral coordinated Mo⁵⁺→Mo⁴⁺(750–900 °C); and (c) Mo⁴⁺→Mo (> 900 °C) [39].
Figure 4. H\textsubscript{2}-temperature-programmed reduction (TPR) patterns of the samples (a–e): SiO\textsubscript{2}, V-Nb/SiO\textsubscript{2}, P-Mo-V/SiO\textsubscript{2}, P-Mo-Nb/SiO\textsubscript{2}, P-Mo-V-Nb/SiO\textsubscript{2}.

The chemical state of Mo and V on the surface of the catalyst has a great influence on the catalytic activity of ethyl lactate to ethyl pyruvate. The energy spectra of V 2p\textsubscript{3/2} and Mo 3d and the results of the fitting curves are shown in Figure 5A,B and Table 3. For comparing, the V-Nb/SiO\textsubscript{2} and P-Mo-V-Nb/SiO\textsubscript{2} has more V\textsuperscript{4+} species than others, which indicates the addition of niobium enhances the degree of reduction of vanadium species. At the same time, it can be observed that the Mo\textsuperscript{5+} species appear on P-Mo-Nb/SiO\textsubscript{2}. The results reveal the interaction of V-Nb and Mo-Nb can enhance the degree of reduction of V\textsubscript{2}O\textsubscript{5} and MoO\textsubscript{3} induced more oxygen vacancies. However, molybdenum in P-containing catalysts mainly exists as Mo\textsuperscript{6+} [22]. Partially reduced vanadium-molybdenum species can lead to more oxygen vacancies, which are beneficial to the improvement of catalytic performance due to vacancies facilitate electron transfer to enhance the adsorption of gaseous oxygen [40,41]. In our case, the V\textsuperscript{4+}/(V\textsuperscript{4++}V\textsuperscript{5+}) ratio increased to 0.68 on P-Mo-V-Nb/SiO\textsubscript{2}, because Mo and Nb oxide components could increase the accessibility and reducibility of VO\textsubscript{x} species [21].

Table 3. Relative chemical composition of catalysts calculated from XPS results

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface Atomic Ratio (%)</th>
<th>Mo\textsuperscript{5+}/(Mo\textsuperscript{5++}Mo\textsuperscript{6+})</th>
<th>V\textsuperscript{4+}/(V\textsuperscript{4++}V\textsuperscript{5+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V-Nb/SiO\textsubscript{2}</td>
<td>-</td>
<td>0.02</td>
<td>0.24</td>
</tr>
<tr>
<td>P-Mo-V/SiO\textsubscript{2}</td>
<td>0.38</td>
<td>0.05</td>
<td>0.48</td>
</tr>
<tr>
<td>P-Mo-Nb/SiO\textsubscript{2}</td>
<td>0.23</td>
<td>0.33</td>
<td>-</td>
</tr>
<tr>
<td>P-Mo-V-Nb/SiO\textsubscript{2}</td>
<td>0.71</td>
<td>0.09</td>
<td>0.68</td>
</tr>
</tbody>
</table>

The spectra of O 1s in catalysts can be shown in Figure 5C. With the increase in the number of supported oxides, it can be observed that the mobility of lattice oxygen become better due to the reduced binding energy (535 eV to 532 eV), which significantly improves the catalyst activity for the conversion of ethyl lactate to ethyl pyruvate. Lattice oxygen on the catalyst surface is consumed in the oxidation reaction, then O\textsubscript{2} in the gas phase is replenished into the vacant site to complete the cycle of oxygen species. Simultaneously the oxygen species, which are located at the surface defects, are more active and therefore more easily reduced [42,43]. The obtained dependence of conversion
rate in ethyl lactate selective oxidation reaction on the concentration of oxygen is in accordance with a MvK redox mechanism, where the irreversible C–H bond activation steps occur on catalyst surface exposing predominantly hydroxyl groups [18]. The high binding energy like V-Nb/SiO₂, the poor circulation of oxygen species during the reaction process leads to deep oxidation for lower selectivity of the target product.

**Figure 5.** XPS spectra and peak fitting results of (A) Mo 3d, (B) V 2p and (C) O 1s signals of the samples (a–e): SiO₂, V-Nb/SiO₂, P-Mo-V/SiO₂, P-Mo-Nb/SiO₂, P-Mo-V-Nb/SiO₂.

### 2.3. Acidic Properties

The surface acidity intensity distribution of the catalyst samples measured by NH₃-TPD is shown in Figure 6. Two weak peaks in range 100–300 °C and 600–800 °C, respectively are observed in the samples, indicative to two types of acidic sites on the surface of samples. However, the first peak may be caused by physical adsorption. When active species are loaded on the support surface, the two types of acidic sites disappear gradually in curve c–e, which implies that the addition of molybdenum and phosphorus could cover acidic sites [44]. This is related to the good dispersion of the active species on the surface of the support. At the same time, weak acidic sites and medium-strong acidic sites appeared on Figure 4c–e, indicating that the catalyst has a wide weak acid distribution on the surface. In short, the acidic sites on the surface have a significant effect on the oxidation of ethyl lactate to ethyl pyruvate. Therefore, the surface acidity of the catalyst is prone to adsorption of ethyl lactate without hydrolysis, and the weak acidic sites and medium-strong acidic sites can promote the desorption of ethyl pyruvate to reduce the rate of hydrolysis reaction, which is beneficial to the selectivity of ethyl pyruvate.

**Figure 7 shows the FTIR spectra of pyridine adsorption of the catalysts, which is carried out to explore the nature of acidic sites and their effects on the selectivity of ethyl pyruvate. The band observed at 1450 cm⁻¹ is characteristics of Lewis acidic sites, and 1488 cm⁻¹ band is related to the coexistence of Brönsted and Lewis acidic sites [37]. The SiO₂ support only has Lewis acidic sites in Figure 4a. It could be observed that Lewis acidic sites and the coexistence of Brönsted and Lewis acidic sites on V-Nb/SiO₂, P-Mo-V/SiO₂, P-Mo-Nb/SiO₂, and P-Mo-V-Nb/SiO₂. However, there is no good difference in the acidity of each catalyst, and the effect on the reaction is not significant. The P-Mo-V-Nb/SiO₂ with the best catalytic performance displayed very weak Lewis and Brönsted acidic sites, and the coexistence of Brönsted and Lewis acidic sites intensity were weaker than others and V-Nb/SiO₂ catalytic activity after it. Therefore, we speculate that the surface acidity of the interaction between V and Nb is favorable for the adsorption of ethyl lactate for conversion.
Figure 6. NH₃-temperature-programmed desorption (TPD) patterns of the samples of (a–e): SiO₂, V-Nb/SiO₂, P-Mo-V/SiO₂, P-Mo-Nb/SiO₂, P-Mo-V-Nb/SiO₂.

Figure 7. Pyridine-FTIR spectra of (a–e): SiO₂, V-Nb/SiO₂, P-Mo-V/SiO₂, P-Mo-Nb/SiO₂, P-Mo-V-Nb/SiO₂. (A): 25 °C; (B): 150 °C; (C): 400 °C

2.4. Catalytic Performance

Figure 8 displays conversion of ethyl lactate and selectivity of ethyl pyruvate product under different reaction temperature. It could be observed that ethyl lactate conversion is positively correlated with reaction temperature. The P-Mo-V-Nb/SiO₂ had a highest conversion, which the conversion of the EL to EP increased from 85% to > 98% when the temperature increased from 220 °C to 280 °C.
As shown in Figure 8B, the ethyl pyruvate selectivity of P-Mo-V/SiO₂ and P-Mo-Nb/SiO₂ was highest at 240 °C and decreased gradually with increasing temperature. The P-Mo-V-Nb/SiO₂ reached to 93% at 260 °C, while the selectivity of V-Nb/SiO₂ began to decrease from 220 °C. We also plotted the yield of major products against ethyl lactate conversion over V-Nb/SiO₂, P-Mo-V/SiO₂, P-Mo-Nb/SiO₂, and P-Mo-V-Nb/SiO₂ at optimized temperature. As shown in Figure 9A, it was observed the worst EP yield at 40% on V-Nb/SiO₂ obviously, which could produce many by-products: ethanol, acetic acid, ethyl acetate, acetaldehyde, and carbon dioxide. In addition, the EP yield of P-Mo-V/SiO₂ and P-Mo-Nb/SiO₂ respectively reached to 49% and 56%, but the P-Mo-V-Nb/SiO₂ increased to 90%. On the basis of these results, we propose a reaction network for the oxidation of ethyl lactate, involving oxidative dehydrogenation, hydrolysis and decarboxylation steps (Figure 9B). In Figure 9A, the total content of acetic acid, acetaldehyde and CO₂ is about the same as ethanol in the reaction on V-Nb/SiO₂, which confirms this reaction network from the side.

Subsequently, the stability of the catalyst samples was investigated while the temperature was fixed at the optimum results (260 °C). The effect of reaction time was studied at different time intervals (Figure 10). The conversion of EL was slightly reduced to 90% over 100 h, while the EP selectivity was lower than 80% from 16 h and continued to decrease to 67%. The result shows that P-Mo-V-Nb/SiO₂ catalyst maintains a high activity for the oxidation of EL, however, the improvement of EP selectivity is further studied for industrial applications in the future.
**Reaction conditions**: amount of all catalysts 1.5 g, temperature 260 °C, LHSV of EL 7.5 h⁻¹, molar ratio of O₂ to EL as 2:1.

**Figure 9.** (A): An overview of product yield at 260 °C reaction temperature over the catalysts of V-Nb/SiO₂, P-Mo-V/SiO₂, P-Mo-Nb/SiO₂, P-Mo-V-Nb/SiO₂. (B): Proposed reaction pathway for the oxidation of ethyl lactate.


2.5. Relationship between Catalyst Structure and Catalytic Performance

The P-Mo-V-Nb/SiO\textsubscript{2} oxides catalyst showed higher ethyl lactate conversion and ethyl pyruvate selectivity in the oxidation of ethyl lactate compared to other catalysts. These could be clarified from the redox properties of the catalysts. H\textsubscript{2}-TPR result revealed that the total reduced amount of active components of the samples descended in the order of P-Mo-V-Nb/SiO\textsubscript{2} > P-Mo-Nb/SiO\textsubscript{2} > P-Mo-V/SiO\textsubscript{2} > V-Nb/SiO\textsubscript{2}. It seemed that the catalytic activity was generally relevant to the rate of hydrogen consumption, which depends on the reducibility of the catalyst. On the other hand, according to the above XRD and Raman results, three highly dispersed phases over the catalysts could be observed: MoO\textsubscript{3}, V\textsubscript{2}O\textsubscript{5}, and Nb\textsubscript{2}O\textsubscript{5}, in which the cooperation of MoO\textsubscript{3} and V\textsubscript{2}O\textsubscript{5} had a good effect on the product selectivity and the Nb\textsubscript{2}O\textsubscript{5} could increase the conversion of ethyl lactate significantly. Oligomeric MoO\textsubscript{X} species can produce by-product such as acetaldehyde [13].

The reactivity and reducibility (Table 4 and Figure 9) reveal that the EP yield is directly proportional to the H\textsubscript{2} consumption of catalysts. The P-Mo-V-Nb/SiO\textsubscript{2} H\textsubscript{2} consumption is at the maximum among all tested samples (Table 4), which accounts for its highest EP yield among these samples. Moreover, the EP yield is improved with the increase of H\textsubscript{2} consumption (Figure 11).

Figure 10. Dependence of EL conversion and EP selectivity on time stream for P-Mo-V-Nb/SiO\textsubscript{2} catalyst at 260 °C.

Figure 11. Correlation between reducibility and the EP yield of the catalysts.
Table 4. Hydrogen consumption of the temperature-programmed reduction (TPR) peaks for the various samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>H₂ Consumption (mmol·g⁻¹) (Temperature before 700 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.04</td>
</tr>
<tr>
<td>V-Nb/SiO₂</td>
<td>1.06</td>
</tr>
<tr>
<td>P-Mo-V/SiO₂</td>
<td>1.53</td>
</tr>
<tr>
<td>P-Mo-Nb/SiO₂</td>
<td>1.48</td>
</tr>
<tr>
<td>P-Mo-V-Nb/SiO₂</td>
<td>1.72</td>
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</tbody>
</table>

In addition, for V-Nb/SiO₂ catalyst, a sharp decrease of the ethyl pyruvate selectivity could be observed, which was attributed to the ethyl pyruvate hydrolysis and decarboxylation to by-products due to Lewis acidic sites of V₂O₅ over the catalyst.

3. Experimental

3.1. Preparation of the Catalyst

A series of SiO₂ supported catalysts were prepared with an equal volume impregnation method. After sufficient impregnation, they were dried at 110 °C and calcined at 600 °C in a muffle furnace. The V-Nb/SiO₂ dipping solution was obtained from 3.2 g of ammonium metavanadate dissolved by the oxalic acid solution which added 1.2 g of niobium ammonium oxalate. The P-Mo-V/SiO₂ dipping solution was obtained from 3.2 g of ammonium metavanadate dissolved by the oxalic acid solution which added 20.6 g of ammonium heptamolybdate tetrahydrate and then 14.5 g of phosphoric acid dropwise. The P-Mo-Nb/SiO₂ dipping solution came from 20.6 g of ammonium heptamolybdate tetrahydrate dissolved adding 1.2 g of niobium ammonium oxalate and 14.5 g of phosphoric acid dropwise. P-Mo-V-Nb/SiO₂ dipping solution was prepared from 3.2 g of ammonium metavanadate dissolved by the oxalic acid solution adding 20.6 g of ammonium heptamolybdate tetrahydrate, 1.2 g of niobium ammonium oxalate, and 14.5 g of phosphoric acid dropwise.

3.2. Catalyst Characterization

The elemental analysis was determined by X-ray fluorescence spectroscopy (XRF) on ZSX Primus II X-ray fluorescence analyzer (Rigaku) using rhodium target X-ray tube (40 kV and 10 mA).

Surface areas were measured with an SSA-6000 analyzer (Biaode Electronic Technology) with the multipoint Brunauer–Emmett–Teller (BET) sorption method.

Powder X-ray diffraction (XRD) was recorded on a Bruker diffractometer (Rigaku) using Cu-Kα radiation (40 kV and 40 mA). Each sample was prepared by gently grinding to powder, and placed into a quartz glass holder for measurement.

Raman spectra were obtained on an inVia (Renishaw) dispersive Raman microscope with a laser wavelength of 532 nm.

H₂-TPR was performed in a ChemiSorb 2720 system (Micromeritics). A sample in a quartz tube was pretreated at 300 °C for 3 h under helium atmosphere. After it was cooled to room temperature, 10% hydrogen in argon substituted the helium until the signal baseline stable. The sample was then heated to 900 °C at a rate of 10 K·min⁻¹. The exhaust gas was detected by a TCD detector after dehydrated by an isopropanol/liquid nitrogen cold trap.

X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250 spectrometer (Thermo Fisher Scientific) using Al-Kα radiation with a pass energy of 30 eV. The binding energies were corrected with respect to C1s peak of contaminated carbon at 284.6 eV.

NH₃-TPD was tested using a ChemBET Pulsar chemisorber (Quantachrome) to determine the acid property of catalyst surfaces. 100 mg of sample was swept in helium at 500 °C for one hour. After being cooled to 50 °C, the sample adsorbed NH₃ adequately. Then helium removed physically
absorped NH3 at 50 °C. It was heated to 850 °C at a rate of 10 K·min⁻¹ in a helium stream, and the signal was detected by a TCD detector after cooled to room temperature.

FT-IR spectra with pyridine adsorption were measured on a Nicolet 6700 spectrometer (Thermo Fisher Scientific) to characterize the acid properties of the catalysts. Before measurement, a sample was tableted as a self-supporting thin wafer. The sample was evacuated in the analysis cell at 400 °C for 2 h to remove water and impurities. After cooled to 25 °C, its infrared spectrum was collected as a background reference. Then, pyridine was introduced to the analysis cell. After about 30 min, the catalyst was saturated by pyridine. Subsequently, pyridine was desorped by evacuation at 25 °C, 150 °C and 400 °C respectively. The FT-IR spectrum of the samples were recorded with the same spectrometer.

3.3. Catalytic Test
The catalysts were evaluated in an atmospheric fixed-bed reactor (inner diameter 8 mm) at 220–280 °C. A catalyst (1 g of catalyst on 0.5 g of SiO₂ support) was placed into the reactor center. Liquid ethyl lactate enters the preheater by constant flux pump and then gas ethyl lactate together with air (molar ratio of O₂ to EL as 2:1) was introduced into the reactor. The liquid hourly space velocity (LHSV) of EL was 7.5 h⁻¹. After the conversion and selectivity were steady, the product exhaust was cooled and collected in an ice water bath. The product was analyzed in a gas chromatograph equipped with an FID detector and a 30QC3/AC20-0.5 capillary column.

4. Conclusions
We developed a quaternary component P-Mo-V-Nb catalyst supported on SiO₂ with an equal volume impregnation method for the selective oxidation of ethyl lactate to ethyl pyruvate. The XRD and N₂ adsorption data between V-Nb and other three phosphorous catalysts suggested high dispersion of active sites under the action of phosphorus. As a result, the highly dispersive sites separated active species, suppressing over oxidation and improving the selectivity. XPS and Raman spectra indicated the existence of MoO₃ to provide higher oxidation for catalyst. The interaction of V and Nb enhanced the degree of reduction of V₂O₅, which may induce more oxygen vacancies, facilitating the transfer of gaseous oxygen to lattice oxygen.

According to the Mars-van Krevelen mechanism, the mobility of lattice oxygen is crucial for the selective oxidative dehydrogenation. Compared with binary V-Nb and ternary P-Mo-V and P-Mo-Nb catalysts, the P-Mo-V-Nb catalyst exhibited the best oxygen mobility according to the H₂-TPR and XPS results. Moreover, the weak acidity of catalyst surface is favorable to avoid the decarboxylation reaction to target a high selectivity of EP. Therefore, the P-Mo-V-Nb/SiO₂ catalyst obtained the maximum yield of 91.8% with a selectivity of 93.8% and a conversion of 99.0% simultaneously at 280 °C. Further study should focus the long-period stability of this P-Mo-V-Nb/SiO₂ catalyst. The proportion of the four elements can be optimized.

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References


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