H₂-Free Gas-Phase Deoxydehydration of 2,3-Butanediol to Butene on SiO₂-Supported Vanadium Catalysts

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Abstract: The gas phase deoxydehydration of 2,3-butanediol to butene was investigated in a plug flow reactor over SiO₂-supported vanadium oxide, γ-alumina, P/ZSM-5 and MgO catalysts with acid/base sites of varying strength. 5V/SiO₂ shows the best performance with 100% conversion and up to 45.2% butene selectivity. The combination of weak acid sites and polymeric VOₓ surface species provides to the 5V/SiO₂ catalyst bifunctional capabilities to achieve dehydrogenation and transfer hydrogenation, allowing it to catalyze the deoxydehydration of 2,3-butanediol to butene even in the absence of H₂. As 2,3-butanediol is a common yet underutilized biomass product, this reaction may provide a viable route for a biomass-to-chemicals application for 2,3-butanediol.

Upgrading of biomass to fuels and chemicals is important for sustainable human development, and intense studies are being carried out to find new technologies to convert the large amount of available bio-derived oxygenates into fuels and chemicals.[11] The vicinal diol 2,3-butanediol (2,3BDO) is a common biomass product synthesized using bacteria sugars derived from biomass feedstock such as corn starch. It has great potential to replace the synthetic 2,3BDO in the market due to its cost-effectiveness compared to the chemical hydrolysis of 2,3-butene. While its isomers such as 1,4-butanediol and 1,3-butadiene have been widely studied for conversion to other chemicals such as tetrahydrofuran and butyrolactone,[12] these cyclization reactions are not available for 2,3BDO due to the vicinal position of its OH groups. Thus, 2,3BDO is much less studied than 1,4- and 1,3-butanediol although it could follow multiple oxidation, reduction and dehydrogenation pathways.[13-6]

The dehydrogenation of 2,3BDO mainly produces butanone (also known as methyl ethyl ketone, MEK) and 2-methylpropanal (MPA) through a E1/E2 mechanism followed by 1,2-rearrangement by hydride and methyl shifts respectively.[2a] This is readily achieved on acid sites, such as those available in phosphate catalysts or zeolites.[3] However, the double dehydrogenation of 2,3BDO to butadiene is more challenging than for 1,4-butanediol because the carbonyl compounds MEK and MPA formed from 2,3BDO are more difficult to dehydrate further compared to enol compounds such as 3-buten-1-ol that are typically formed from 1,4-butanediol.[4] Alternatively, Zheng et al. recently reported a Cu/ZSM5 catalyst that converts 2,3BDO to butene in the presence of excess H₂, without further hydrogenation to butane.[5]

In this study, the gas phase conversion of 2,3BDO was carried out over SiO₂-supported vanadium oxide, γ-alumina, P/ZSM-5 and MgO catalysts with acid/base sites of varying strength. We show that a deoxydehydration pathway of 2,3BDO to butene in the absence of H₂ exists, via a hydrogen donor mechanism from 2,3BDO to MEK over vanadium oxide (VOₓ) surface sites.

Table 1. N₂ physisorption data, NH₃-TPD data, acid site density, and calculated V surface density for the various acid catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>1V/SiO₂</th>
<th>5V/SiO₂</th>
<th>10V/SiO₂</th>
<th>γ-alumina</th>
<th>P/ZSM5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area [m²/g]</td>
<td>305</td>
<td>251</td>
<td>187</td>
<td>130</td>
<td>365</td>
</tr>
<tr>
<td>NH₃ adsorbed [µmol/g]</td>
<td>829</td>
<td>1893</td>
<td>2211</td>
<td>1126</td>
<td>532</td>
</tr>
<tr>
<td>Acid sites density [sites/nm²]</td>
<td>1.64</td>
<td>4.54</td>
<td>7.12</td>
<td>5.22</td>
<td>0.88</td>
</tr>
<tr>
<td>V surface density [V/nm³]</td>
<td>0.38</td>
<td>2.24</td>
<td>6.01</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The ammonia temperature-programmed desorption (NH₃-TPD) and N₂ physisorption data for the vanadia-silica catalysts and various acid catalysts are shown in Table 1 and Fig. 1a. As vanadia loading increases from 1 to 10% on SiO₂, the surface area and pore volume decreases, which suggests that vanadia nanoparticles are uniformly filling the pores of SiO₂. V/SiO₂ catalysts exhibit weak acidity indicated by the lower temperature NH₃-TPD peaks located from 120 to 150 °C. The amount of acid sites increases with the vanadium loading. In addition, the IR spectra of pyridine-adsorbed V/SiO₂ catalysts at 200 °C show that the majority of acid sites on the vanadium catalyst are Lewis acid sites, as indicated by the peak at 1449 cm⁻¹ (Fig S1). The P/ZSM5 catalyst has a major temperature peak at 250 °C. γ-alumina has both a low temperature peak at 130 °C and a broad peak from 250-400 °C, which indicates the existence of two kinds of acid sites.

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Supporting information for this article is given via a link at the end of the document.
It is well known that there are three main types of vanadia species present on silica surfaces, depending on dispersion and loading: bulk-like octahedrally-coordinated $\text{V}_2\text{O}_5$, tetrahedrally-coordinated polymeric $\text{VO}_x$ (with two bridging $\text{V-O-V}$ bonds, one $\text{V}=\text{O}$ bond and one $\text{V}-\text{O-support bond}$) and monomeric $\text{VO}_x$ (with one $\text{V}=\text{O}$ bond and three $\text{V}-\text{O-support bonds}$) species (Fig. S2). The X-ray diffraction (XRD), UV-visible, and Raman spectra of V/SiO$_2$ catalysts are shown in Fig. 1b-d. The XRD peaks of crystalline $\text{V}_2\text{O}_5$ (JCPDS # 001-0359) are present in 10V/SiO$_2$ catalyst but they are not obvious in 5V/SiO$_2$ and invisible on 1V/SiO$_2$ catalysts due to the low loading and/or lack of crystallinity. Consistently, Raman spectra shows that $\text{V}_2\text{O}_5$ crystallites (indicated by the 144, 283, 405, 490, 526, 699 and 993 cm$^{-1}$ peaks) are dominant on 10V/SiO$_2$. The intensities of these peaks reduce and the full width at half maximum increase with decreasing loading of V, suggesting that crystalline $\text{V}_2\text{O}_5$ is present with smaller grain sizes on 5V and 1V compared to 10V/SiO$_2$. In addition, two Raman spectra bands attributed to monomeric $\text{VO}_x$ (912 cm$^{-1}$ band) and polymeric (1032 cm$^{-1}$ band) surface $\text{VO}_x$ species are observed on the samples with 1% and 5% loadings, while becoming very weak at 10% loading. The UV-visible spectrum shows two main peaks. The first peak at 3.2 eV corresponds to a combination of bulk-like $\text{V}_2\text{O}_5$ and polymeric $\text{VO}_x$, while the second peak at 4.9 eV corresponds to a combination of polymeric $\text{VO}_x$ and monomeric $\text{VO}_x$ species. While the 3.2 eV and 4.9 eV peaks have approximately the same relative intensity for 1% and 5% loading, the 3.2 eV peak is much more intense than the 4.9 eV peak for 10% loading, indicating that bulk-like $\text{V}_2\text{O}_5$ dominates at higher loading. These results are in agreement with the V surface densities shown in Table 1 and with previous studies showing that isolated $\text{VO}_x$ species are present at surface densities of <1 V/nm$^2$, monovanadate and polyvanadate $\text{VO}_x$ species are present from 1.2-4.4 V/nm$^2$, and $\text{V}_2\text{O}_5$ is formed at >4.4 V/nm$^2$. From the analysis above, it can be concluded that monomeric $\text{VO}_x$, polymeric $\text{VO}_x$, and probably small grains of bulk-like $\text{V}_2\text{O}_5$ exist at 1% and 5% loading, while bulk-like $\text{V}_2\text{O}_5$ dominates at 10% loading.

Figure 2 shows the conversion of 2,3BDO and product selectivities for the investigated catalysts. It should be noted that no conversion of 2,3-BDO was observed for the non-catalyzed reaction performed in a blank tube under the same conditions. The catalysts with relatively stronger acid sites ($\gamma$-alumina and P/ZSM5) produce mostly MEK and MPA via dehydrogenation, in agreement with previous studies. The total selectivity of MEK and MPA is up to 87% on P/ZSM5 while the selectivity to butene is only 2%. The $\gamma$-alumina catalyst which contains both weak and strong acid sites (NH$_3$ desorption peaks at 130 °C and 247 °C, respectively) produces slightly more butene and MEK than the P/ZSM5 catalyst, containing stronger acid sites (NH$_3$ desorption peaks at 250 °C). The stronger acid sites on the P/ZSM5 increase isomerization of MEK to 2-methylpropanal and also result in more cracking products, C1-C3 alkanes and alkenes, in agreement with previous studies.

On the other hand, the basic MgO catalyst is neither very active for BDO conversion (29.5%) nor selective to 2-butanol (19.7%) and butene (4.2%). However, it has high selectivity to acetoin (27.2%) from the dehydrogenation of 2,3-butanediol, while the selectivity of MEK and MPA greatly decreases to less than 40%. Clearly, the MgO catalyst does not have the acid sites required to completely dehydrate 2,3BDO and 2-butanol. Indeed acetoin and 2-butanol are almost undetectable on the acid catalysts in this study. The simultaneous presence of MEK, acetoin and 2-butanol suggests that 2-butanol is produced by the transfer of hydrogen from 2,3BDO to MEK, which will be further discussed later.

On the three vanadia catalysts, butene selectivity is at least 5 times higher than on the other catalysts at 400 °C. The highest conversion and selectivity to butene is observed for 5% wt. loading with 100% conversion and 45.2% total selectivity to butene at 500 °C. The volcano-type behavior in catalytic performance with increasing vanadium loading has previously
been observed in other vanadium-catalyzed reactions, such as benzene hydroxylation.\textsuperscript{[10]} Similar to those previous studies, the maximum in catalytic performance of our 5V/SiO\textsubscript{2} catalyst correlates well with its maximum in surface monomeric VO\textsubscript{2}/polymeric VO\textsubscript{2} species at 5% loading. Only trace amounts of butanol (<0.1%) can be detected on the vanadium catalysts, most likely due to its rapid dehydration to butene on the acid sites. The ratio of the three isomers is different on these three vanadia catalysts and the values differ significantly from the equilibrium distribution, suggesting that they are the primary products and secondary isomerization of butene does not occur.\textsuperscript{[11]} It is interesting to note that more than 10% selectivity to acetaldehyde and diacetyl (from double dehydration of 2,3-DBD) is observed on these vanadia catalysts while it is not observed on the basic MgO catalyst and only trace amounts are observed on strong acidic catalysts, Al\textsubscript{2}O\textsubscript{3} and P/ZSM5(30). The acetaldehyde is likely to have been produced from the C-C cleavage of acetoin on the weak acid sites, since the MgO catalyst discussed previously produces acetoin instead, which can be ascribed to the absence of acid sites.

This combination of dehydration (MEK, MPA), dehydrogenation (acetaldehyde, acetoin and diacetyl) and hydrogenation (2-butanol) products on the vanadium catalysts in absence of external H source suggests that transfer hydrogenation between 2,3-butanediol and MEK occurs on the vanadium catalysts.\textsuperscript{[12]} MEK gains two hydrogen atoms to form 2-butanol, which then dehydrates to form butene, while 2,3-butanediol loses two hydrogen atoms to form acetoin, which can either lose another two hydrogen atoms to form diacetyl or undergo C-C cleavage to form two molecules of acetaldehyde. Transfer hydrogenation reactions involving different ketones (hydrogen acceptor) and alcohols (hydrogen donor) in both liquid and gas phases have been previously demonstrated over various catalysts, even between MEK and 2-propanol.\textsuperscript{[12a] 13} Since 2,3-DBD is a vicinal diol (hydrogen donor) that dehydrates to form MEK (a hydrogen acceptor ketone), the use of secondary hydrogen donors for MEK is not required, allowing 2,3-DBD to be directly deoxyhydrated to butene on the VO\textsubscript{2} sites without external reductants. The high yield of MEK suggests that this transfer hydrogenation is the rate-limiting step in the reaction pathway. Furthermore, no butane was observed, which suggests that transfer hydrogenation in this reaction pathway is preferential to C=O hydrogenation instead of C=C hydrogenation. The low ratio of acetaldehyde to butene, for example in the 5V/SiO\textsubscript{2} catalyst (13.7% acetaldehyde versus 37% butene), suggests that acetaldehyde could undergo further reactions. Acetaldehyde could undergo steam reforming by reacting with water molecules produced from the two dehydration reactions. Indeed, previous studies of other silica-supported metal oxide have shown that mainly hydrogen and carbon dioxide, with trace amounts of CH\textsubscript{4}, CO and propylene, can be produced.\textsuperscript{[10, 14]} This is supported by the detection of CO\textsubscript{2} in the outlet stream using the TCD detector of the GC, as well as 0.5% and 1.7% of CH\textsubscript{4} at higher reaction temperatures, 450 °C and 500 °C, respectively for the 5V/SiO\textsubscript{2} catalyst. The hydrogen produced from acetaldehyde steam reforming could have further contributed to the hydrogenation of the MEK intermediate. Further investigation of the effect of temperature on the high-performing 5V/SiO\textsubscript{2} catalyst (Fig. 2) indicates that temperature has a significant effect the selectivity to butene. 100% conversion is reached at 350 °C and above, while butene selectivity increases from 24.6% to 45.2% as the reaction temperature is increased from 250 °C to 500 °C.

To verify the transfer hydrogenation mechanism, in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was conducted on the 5V/SiO\textsubscript{2} catalyst with chemisorbed 2,3BD (Fig. 3). When 2,3-butanediol is adsorbed onto the catalyst, the C-O stretch bands (1292 cm\textsuperscript{-1}), O-H stretch band (3200-3600 cm\textsuperscript{-1}), C-H stretch bands (2902, 2942, 2987 cm\textsuperscript{-1}) of 2,3BD is readily observed at 30 °C. At 100 °C, the C=O stretch band (1700 cm\textsuperscript{-1}) of MEK is observed. At 300-500 °C, alkene bands such as the =C-H stretch at 3217 cm\textsuperscript{-1}, =C-H bend (920 cm\textsuperscript{-1}) and the C=C stretch at 1640 cm\textsuperscript{-1} indicate the presence of butene.\textsuperscript{[18]}

![Figure 3. In-situ FTIR (DRIFTS) results of 2,3BD adsorbed on 5V/SiO\textsubscript{2}.](image)

### Table 2. Major products from intermediates testing at 400 °C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Feed</th>
<th>Major Products Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5V/SiO\textsubscript{2}</td>
<td>2,3BD + H\textsubscript{2}</td>
<td>37% butene, 41% MEK, 14% acetaldehyde</td>
</tr>
<tr>
<td>5V/SiO\textsubscript{2}</td>
<td>MEK + H\textsubscript{2}</td>
<td>3% butene, 0.6% 2-butanol</td>
</tr>
<tr>
<td>5V/SiO\textsubscript{2}</td>
<td>2-butanol</td>
<td>100% butene</td>
</tr>
<tr>
<td>5P/SiO\textsubscript{2}</td>
<td>MEK + H\textsubscript{2}</td>
<td>19% 2-butanol, 11% butane, 1% butene</td>
</tr>
</tbody>
</table>

Additionally, various reaction intermediates were used as feedstock on the 5V/SiO\textsubscript{2} catalyst and on a 5Pt/SiO\textsubscript{2} standard hydrogenation catalyst (Table 2) to verify the reaction pathways. When the reaction was performed under a gaseous mixture of N\textsubscript{2} and H\textsubscript{2} with a molar ratio of 1:1 using the same gas flow rate (40 ml/min), the 5V/SiO\textsubscript{2} catalyst produces the same product distribution as when the reaction was carried out in pure N\textsubscript{2}. Furthermore, when MEK and H\textsubscript{2} are used as feedstock, a very low conversion of MEK to butene and 2-butanol is observed, which can be easily explained since the activation of H\textsubscript{2} on 5V/SiO\textsubscript{2} is very weak. When the 5V/SiO\textsubscript{2} catalyst was tested using 2-butanol as feedstock, 100% selectivity to butene (with
similar butene isomers distribution as when the reaction was performed with 2,3BDO as reactant) is observed, which indicates that this reaction pathway can be easily achieved. This is consistent with previous studies of butanediol dehydration over solid acid catalysts.\textsuperscript{[16]}

When MEK and H₂ were used as feedstock on the 5Pt/SiO₂ hydrogenation catalyst, 2-butanol, butane and trace amounts of butene are observed. This suggests that the presence of a hydrogen donor (in this case activated H₂ on Pt) would hydrogenate to form 2-butanal, but due to the lack of acid sites on the Pt/SiO₂ sample, 2-butanol is only partially dehydrated. In addition, due to the strong hydrogenation activity of Pt, most of the butene formed from dehydration of 2-butanol is further hydrogenated to butane.\textsuperscript{[17]}

Lastly, we have also varied the weight hourly space velocity (WHSV) for the 5V/SiO₂ catalyst. As WHSV is increased from 1.5 h\(^{-1}\) to 59 h\(^{-1}\) (Figure S3), conversion of 2,3-butanediol decreases as expected. In addition, at high WHSV, we observe an increase in intermediates (MEK, MPA, acetoin, butanol) and a decrease in final products (butene, acetaldehyde). The ratio of MEK/butene increases with WHSV, suggesting that MEK is the primary intermediate and the transfer hydrogenation from 2,3BDO to MEK to form 2-butanol is the rate-limiting step.

Based on our results, a reaction pathway can be proposed (Scheme 1), which accounts for the product distribution observed on the 5V/SiO₂ catalyst. 2,3BDO first undergoes dehydration to form butanone (MEK) on both acidic and basic catalysts. Then, 2,3BDO transfers hydrogen to MEK, likely through an intermediate step involving the partial reduction of VO\(_x\) species by 2,3-butanediol, similarly as reported in previous studies showing the reduction of well-dispersed WO\(_x\) sites by 2-butanol and a hydride transfer from 2,3-butanediol to MEK, as previously reported using homogeneous catalysts with deuterated alcohol as hydrogen donor for transfer hydrogenation of ketones.\textsuperscript{[11, 12]} This transfer hydrogenation reaction forms 2-butanol and acetoin, where acetoin can subsequently undergo C-C cleavage to form acetaldehyde or undergo another dehydration to form diacetyl. Lastly, 2-butanol undergoes another dehydration to form the butene isomers (1-butene, trans-2-butene and cis-2-butene) as primary products. This reaction mechanism is similar to that proposed by Zheng et al. for the conversion of 2,3-butanediol to butene in the presence of excess H\(_2\).\textsuperscript{[9]} The key difference here is that vanadia catalyst is able to intrinsically hydrogenate MEK without requiring an external source of H\(_2\), by transferring hydrogen from the 2,3BDO reactant to the MEK intermediate.\textsuperscript{[30]}

In summary, we have demonstrated the conversion of 2,3BDO to butene in the absence of H\(_2\). The 5V/SiO₂ catalyst synthesized by a simple incipient wetness impregnation gives the highest performance for gas-phase conversion of 2,3BDO to butene, with up to 100% 2,3BDO conversion and 45% selectivity to butene. The proposed reaction pathway involves a dehydration-hydrogenation-dehydration pathway, with MEK and 2-butanol as intermediates. The use of 2,3-butanediol for transfer hydrogenation with its own dehydration product (MEK) allows for high selectivity towards butene and the selective hydrogenation of the C=O bond of MEK without the need for additional hydrogen sources. The presence of the MEK intermediate in the product stream suggests that the transfer hydrogenation is the rate-limiting step, and fine-tuning the acid and VO\(_x\) sites may further improve the butene selectivity.

**Experimental Section**

Commercial γ-alumina and MgO were obtained from Sigma. 1V/SiO₂, 5V/SiO₂, 10V/SiO₂, 5Pt/SiO₂ and P/ZSM5(30) (prefix indicates wt % loading) were synthesized by incipient wetness impregnation method. Ammonium metavanadate and tetraamineplatinum(II) nitrate were used as precursors with fumed SiO₂ as support followed by calcination. P/ZSM5(30) was synthesized by a previously-reported method at 20% P loading.\textsuperscript{[16]} Catalyst testing was performed in a 1/4" stainless steel packed bed reactor at atmospheric pressure using a WHSV of 1.5 h\(^{-1}\). The products were analyzed through online gas chromatography with an Agilent 7890A GC equipped with FID and TCD detectors. Further details of catalyst preparation, characterization and testing are available in the Supporting Material.

**Acknowledgements**

This work was supported by the Institute of Chemical and Engineering Sciences (A*STAR), project ICES/14-214A02.

**Keywords:** vanadium oxide • 2,3-butanediol • butene • deoxydehydration • transfer hydrogenation
Deoxydehydration without external H₂: 2,3-butanediol can be selectively deoxydehydrated to butene on SiO₂-supported vanadium catalysts without the presence of external H₂. This involves multiple dehydrations and transfer hydrogenation from 2,3-butanediol to its intermediate butanone, a pathway attributed to the combination of weak acid sites and surface polymeric VO₂ species.

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