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H_2-Free Gas-Phase Deoxydehydration of 2,3-Butanediol to Butene on SiO_2-Supported Vanadium Catalysts

Kelvin Mingyao Kwok[a,b], Catherine Kai Shin Choong[a], Daniel Sze Wei Ong[a], Joy Chun Qi Ng[a], Chuandayani Gunawan Gwie[a], Luwei Chen,*[a] and Armando Borgna[a]

Abstract: The gas phase deoxydehydration of 2,3-butanediol to butene was investigated in a plug flow reactor over SiO_2-supported vanadium oxide, γ-alumina, P/ZSM-5 and MgO catalysts with acid/base sites of varying strength. 5V/SiO_2 shows the best performance with 100% conversion and up to 45.2% butene selectivity. The combination of weak acid sites and polymeric VO_x surface species provides to the 5V/SiO_2 catalyst bifunctional capabilities to achieve dehydration and transfer hydrogenation, allowing it to catalyze the deoxydehydration of 2,3-butanediol to butene even in the absence of H_2. 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.[1] 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.[1c] 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 oxide. While its other isomers such as 1,4-butanediol and 1,3-butanediol have been widely studied for conversion to other chemicals such as tetrahydrofuran and butyrolactone,[2] 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 dehydration pathways.[1c-d]

The dehydration 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 dehydration 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 H_2, without further hydrogenation to butane.[5]

In this study, the gas phase conversion of 2,3BDO was carried out over SiO_2-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 H_2 exists, via a hydrogen donor mechanism from 2,3BDO to MEK over vanadium oxide (VO_x) surface sites.

Table 1. N_2 physisorption data, NH_3-TPD data, acid site density, and calculated V surface density for the various acid catalysts.

Catalyst	1V/SiO_2	5V/SiO_2	10V/SiO_2	γ-alumina	P/ZSM5
Surface area [m^2/g]	305	251	187	130	365
NH_3 adsorbed [μmol/g]	829	1893	2211	1126	532
Acid sites density [sites/nm^2]	1.64	4.54	7.12	5.22	0.88
V surface density [V/nm^2]	0.38	2.24	6.01	-	-

The ammonia temperature-programmed desorption (NH_3-TPD) and N_2 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 SiO_2, the surface area and pore volume decreases, which suggests that vanadia nanoparticles are uniformly filling the pores of SiO_2. V/SiO_2 catalysts exhibit weak acidity indicated by the lower temperature NH_3-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/SiO_2 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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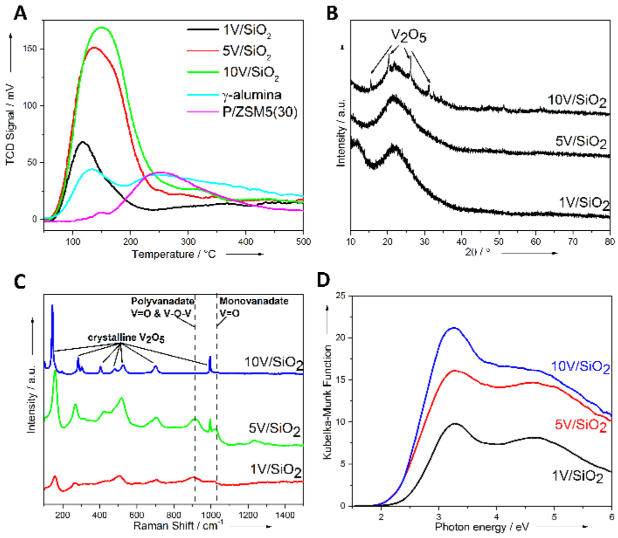

Figure 1. a) NH_3-TPD profile of various acid catalysts; b) XRD, c) Raman, and d) UV-visible spectra of $1V/SiO_2$, $5V/SiO_2$ and $10V/SiO_2$.

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 V_2O_5, tetrahedrally-coordinated polymeric VO_x (with two bridging V-O-V bonds, one V=O bond and one V-O-support bond) and monomeric VO_4 (with one V=O bond and three V-O-support bonds) species (Fig. S2).[6] 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 V_2O_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 V_2O_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 V_2O_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 VO_4 (912 cm^{-1} band) and polymeric (1032 cm^{-1} band) surface VO_x species are observed on the samples with 1% and 5% loadings, while becoming very weak at 10% loading.[7] The UV-visible spectrum shows two main peaks. The first peak at 3.2 eV corresponds to a combination of bulk-like V_2O_5 and polymeric VO_x, while the second peak at 4.9 eV corresponds to a combination of polymeric VO_x and monomeric VO_4 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 V_2O_5 dominates at higher loading.[6a] These results are in agreement with the V surface densities shown in Table 1 and with previous studies showing that isolated VO_x species are present at surface densities of <1 V/nm^2, monovanadate and polyvanadate VO_x species are present from 1.2-4.4 V/nm^2, and V_2O_5 is formed at >4.4 V/nm^2.[8] From the analysis above, it can be concluded that monomeric VO_4, polymeric VO_x and probably small grains of bulk-like V_2O_5 exist at 1% and 5% loading, while bulk-like V_2O_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 condition. The catalysts with relatively stronger acid sites (γ-alumina and P/ZSM5) produce mostly MEK and MPA via dehydration, in agreement with previous studies.[2a] The total selectivity of MEK and MPA is up to 87% on P/ZSM5 while the selectivity to butene is only 2%. The γ-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.[9]

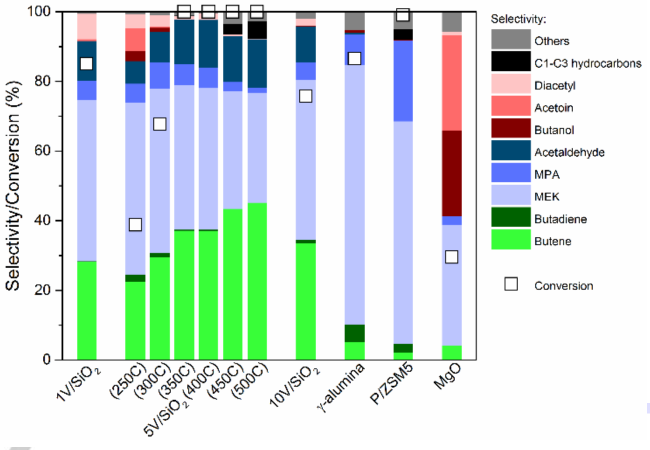

Figure 2. Product distribution for 2,3BDO hydrodeoxygenation over $1V/SiO_2$, $5V/SiO_2$, $10V/SiO_2$, γ-alumina, P/ZSM-5 and MgO catalysts. Reaction conditions: 2,3BDO (0.010 ml/min), N_2 carrier gas (40 ml/min), catalyst (0.4 g), temperature (400 °C unless otherwise stated), atmospheric pressure.

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

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been observed in other vanadium-catalyzed reactions, such as benzene hydroxylation.[10] Similar to those previous studies, the maximum in catalytic performance of our 5V/SiO_2 catalyst correlates well with its maximum in surface monomeric VO_4/polymeric VO_x 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.[11] It is interesting to note that more than 10% selectivity to acetaldehyde and diacetyl (from double dehydrogenation of 2,3BDO) 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_2O_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.[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.[12a,13] Since 2,3BDO 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 2,3BDO to be directly deoxydehydrated to butene on the VO_x 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_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_4, CO and propylene, can be produced.[1b, 14] This is supported by the detection of CO_2 in the outlet stream using the TCD detector of the GC, as well as 0.5% and 1.7% of CH_4 at higher reaction temperatures, 450 °C and 500 °C, respectively for the 5V/SiO_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_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_2 catalyst with chemisorbed 2,3BDO (Fig. 3). When 2,3-butanediol is adsorbed onto the catalyst, the C-O stretch bands (1292 cm^{-1}), O-H stretch band (3200-3600 cm^{-1}), C-H stretch bands (2902, 2942, 2987 cm^{-1}) of 2,3BDO is readily observed at 30 °C. At 100 °C, the C=O stretch band (1700 cm^{-1}) of MEK is observed. At 300-500 °C, alkene bands such as the =C-H stretch at 3217 cm^{-1}, =C-H bend (920 cm^{-1}) and the C=C stretch at 1640 cm^{-1} indicate the presence of butene.[15]

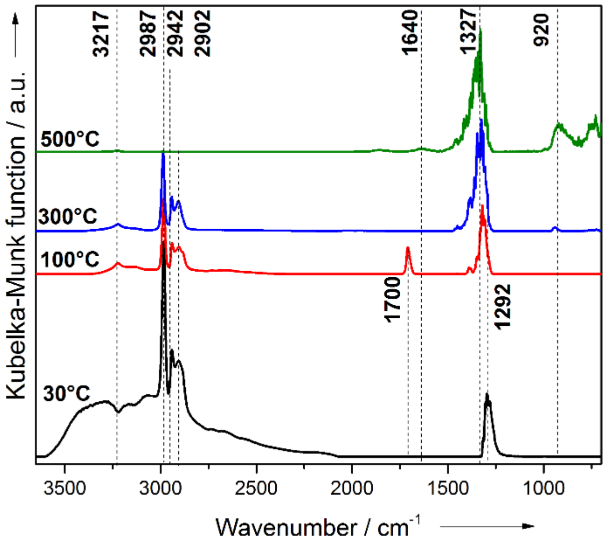


Figure 3. In-situ FTIR (DRIFTS) results of 2,3BDO adsorbed on 5V/SiO_2.

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

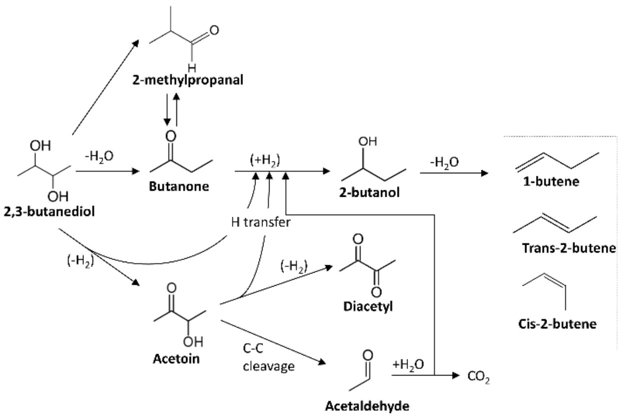
Catalyst	Feed	Major Products Yield (%)
5V/SiO_2	2,3BDO + H_2	37% butene, 41% MEK, 14% acetaldehyde
5V/SiO_2	MEK + H_2	3% butene, 0.6% 2-butanol
5V/SiO_2	2-butanol	100 % butene
5Pt/SiO_2	MEK +H_2	19% 2-butanol, 11% butane, 1% butene

Additionally, various reaction intermediates were used as feedstock on the 5V/SiO_2 catalyst and on a 5Pt/SiO_2 standard hydrogenation catalyst (Table 2) to verify the reaction pathways. When the reaction was performed under a gaseous mixture of N_2 and H_2 with a molar ratio of 1:1 using the same gas flow rate (40ml/min), the 5V/SiO_2 catalyst produces the same product distribution as when the reaction was carried out in pure N_2. Furthermore, when MEK and H_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_2 on 5V/SiO_2 is very weak. When the 5V/SiO_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 butanol dehydration over solid acid catalysts.[16]

When MEK and H_2 was used as feedstock on the 5Pt/SiO_2 hydrogenation catalyst, 2-butanol, butane and trace amounts of butene are observed. This suggests that MEK in the presence of a hydrogen donor (in this case activated H_2 on Pt) would hydrogenate to form 2-butanol. Due to the lack of acid sites on the Pt/SiO_2 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.[17]

Lastly, we have also varied the weight hourly space velocity (WHSV) for the 5V/SiO_2 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/SiO_2 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.[11, 12a] This transfer hydrogenation reaction forms 2-butanol and acetoin, where acetoin can subsequently undergo C-C cleavage to form acetaldehyde or undergo another dehydrogenation 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[5], 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.[3b]



Scheme 1. Proposed reaction pathway from 2,3-butanediol to butene.

In summary, we have demonstrated the conversion of 2,3BDO to butene in the absence of H_2. The 5V/SiO_2 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/SiO_2, 5V/SiO_2, 10V/SiO_2, 5Pt/SiO_2 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 SiO_2 as support followed by calcination. P/ZSM5(30) was synthesized by a previously-reported method at 20% P loading.[18] 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

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Keywords: vanadium oxide • 2,3-butanediol • butene • deoxydehydration • transfer hydrogenation

[1] a) G. W. Huber, R. D. Cortright, J. A. Dumesic, *Angew. Chem. Int. Ed.* **2004**, *43*, 1549-1551; b) M. E. Sad, M. Neurock, E. Iglesia, *J. Am. Chem. Soc.* **2011**, *133(50)*, 20384-20398**;** c) X. Ji, H. Huang, P. Ouyang, *Biotechnol. Adv.* **2011**, *29(3)*, 351-364; d)
[2] a) E. V. Makshina, M. Dusselie, W. Janssens, J. Degrève, P.A. Jacobs, B.F. Sels, *Chem. Soc. Rev.* **2014**, *43*, 7917-7953; b) M. A. Nikitina, I. I. Ivannova, *ChemCatChem* **2016**, *8*, 1346 – 1353.
[3] a) J. Lee, J. B. Grutzner, W. E. Walters, W. N. Delgass, *Stud. Surf. Sci. Catal.* **2000**, *130*, 2603-2608; b) J. Zhao, D. Yu, W. Zhang, Y. Hu, T. Jiang, J. Fu, H. Huang, *RSC Adv.* **2016**, *6*, 16988; c) D. W. Hwang, P. Kashinathan, J. M. Lee, J. H. Lee, U. Lee, J. Hwang, Y. K. Kwang, J. Chang, *Green Chem.* **2011**, *13*, 1672-1675.
[4] S. D. Blass, C. Rosenthal, A. Bhan, L. D. Schmidt, *Catal. Commun.* **2013**, *42*, 54-57.
[5] Q. Zheng, W. D. Wales, M. G. Heidlage, M. Rezac, H. Wang, S. H. Bossmann, K. L. Hohn, *J. Catal.* **2015**, *330*, 222-237.
[6] a) B. M. Weckhuysen, D. E. Keller, *Catal. Today* **2003**, *78*, 25-46; b) I. E. Wachs, *Dalton Trans.* **2013**, *42*, 11762.
[7] A. Khodakov, B. Olthof, A. T. Bell, E. Iglesia, *J. Catal.* **1999**, *181*, 205-216.
[8] S. D. Jackson, S. Rugmini, *J. Catal.* **2007**, *251*, 59-68.
[9] N. Xue, X. Chen, L. Nie, X. Guo, W. Ding, Y. Chen, M. Gu, Z. Xie, *J. Catal.* **2007**, *248*, 20-28.
[10] a) Y. Fu, H. Ma, Z. Wang, W. Zhu, T. Wu, G. Wang, *J. Mol. Catal. A: Chem* **2004**, *221*, 163-168; b) P. R. Makgwane, S. S. Ray, *Appl. Catal., A* **2015**, *492*, 10-22.
[11] a) C. D. Baertsch, K. T. Komala, Y. H. Chua, E. Iglesia, *J. Catal.* **2002**, *205*, 44-57; b) J. Backvall, *J. Organomet. Chem.* **2002**, *652*, 105-111
[12] a) C. L. Kibby, W. K. Hall, *J. Catal.* **1973**, *31*, 65-73; b) A. L. Denning, H. Dang, Z. Liu, K. M. Nicholas, F. C. Jentoft, *ChemCatChem* **2013**, *5*, 3567-3570.
[13] a) M. Bartok, G. Szollosi, *React. Kinect. Catal. Lett.* **1999**, *68(*2), 197-205; b) G. Szollosi, M. Bartok, *Catal. Lett.* **1999**, *59*, 179-185. c) H. C. Maytum, B. Tavassoli, J. M. J. Williams, *Org. Lett.* **2007**, *9(21)*, 4387-4389; d) C. Aellig, F. Jenny, D. Scholz, P. Wolf, I. Giovinazzo, F. Kollhoff, I. Hermans, *Catal. Sci. Technol.* **2014**, *4*, 2326-2331.
[14] E. Seker, *Int. J Hydrogen Energy* **2008**, *33*(8), 2044-2052.
[15] N. H. Li, S. Sun, *J. Electroanal. Chem.* **1998**, *448*, 5-15.
[16] R. M. West, D. J. Braden, J. A. Dumesic, *J. Catal.* **2009**, *262*, 134-143.
[17] N. Li, G. W. Huber, *J. Catal.* **2010**, *270*, 48-59.
[18] K. Ramesh, C. Jie, Y. Han, A. Borgna, *Ind. Eng. Chem. Res.* **2010** *49(9)*, 4080-4090.

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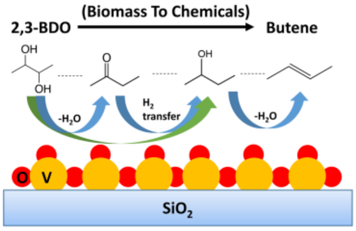
Entry for the Table of Contents

COMMUNICATION

Deoxydehydration without external H_2: 2,3-butanediol can be selectively deoxydehydrated to butene on SiO_2-supported vanadium catalysts without the presence of external H_2. 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 VO_x species.



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