

Selective Electrochemical Conversion of Biomass-derived Valeric Acid to Ethers/Esters

Yuchen liu¹, Gang Yuan¹, Xiaona Ren¹ and Qingfa Wang^{1,2,*}

¹ Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P. R. China

² Collaborative Innovation Centre of Chemical Science and Engineering (Tianjin), Tianjin University, Tianjin 300072, P. R. China

*E-mail: qfwang@tju.edu.cn

Received: 29 December 2017 / Accepted: 13 February 2018 / Published: 6 March 2018

To quantitatively convert biomass into value-added chemicals or biofuels is still a great challenge. Herein, we develop an efficient electrochemical method to convert the biomass-derived valeric acid into ethers (butyl methyl ether and butyraldehyde dimethyl acetal) or esters (methyl valerate) on boron-doped diamond (BDD) electrode in methanol solution. The products distribution was well controlled by tuning the supporting electrolyte and the KOH amount. 98.7% selectivity and ca. 58% Faraday efficiency for ethers and 96% selectivity for esters were achieved by optimizing the supporting electrolytes, initial molar ratio of VA to KOH, VA feed concentration and anodic potential. Strong alkali as supporting electrolyte, high VA feed concentration and initial VA/KOH=1 (mol/mol) favoured the formation of ether products. Fatty acid methyl esters were high-selectively (>96%) produced by using NaClO₄ as the supporting electrolyte and/or adding excessive KOH (initial KOH/VA ratio beyond 2:1). Moreover, partially replacing methanol with ethanol, only one new diether (1,1-diethoxybutane) was formed. A rational mechanism of synthetic butyraldehyde dimethyl acetal via electrocatalytic decarboxylation, rearrangement of carbenium ion, Aldol reaction on BDD in alcohols solution was developed. This strategy may provide a new direction for renewable chemicals and fuels from biomass.

Keywords: Valeric acid; electrochemistry; catalysis; selective conversion

1. INTRODUCTION

Developing clean, renewable and sustainable fuels and chemicals has become more and more urgent due to the depleting of petroleum resources, energy security and environmental problems (CO₂ emissions and greenhouse gas)[1,2]. Lignocellulosic biomass has become one of the most promising options to produce the environmentally friendly and sustainable fuels and chemicals due to its

inedibility, fast renewability and low cost [3-5]. Recently, with lignocellulose as a raw material, Valeric acid (VA) has been considered as an important renewable (lignocellulose-derived) platform compound [6,7] and has attracted significant attention[6-11].

Much work have been done on conversion of VA to renewable fuels. For example, VA is the key intermediate in the conversion of LA to valeric acid esters, which are considered to be a new class of cellulosic biofuels[8-10]. As an alternative to the esterification, carboxylic acid ketonization has become one of the promising ways to decrease the oxygen content of products with an extended carbon chain. Different oxide catalysts (such as $Ce_{0.5}Zr_{0.5}O_2$, CeO_2/Al_2O_3 , MnO_2/Al_2O_3 , MnO_2/ZrO_2 , CeO_2/TiO_2 , MnO_2/TiO_2) have been widely studied to enhance the conversion of VA into ketones via ketonic decarboxylation[7, 12-16]. VA could also be converted into C9 alkane sequentially passing throughout two single-bed reactor: (1) ketonization with CO_2 and H_2O release, and (2) hydrodeoxygenation over Pt-based catalysts with H_2O elimination[7]. Corma *et al* [17] investigated the production of kerosene from VA in a two-bed continuous reactor in the presence of hydrogen. High selectivity and good yield of *n*-nonane from VA was obtained by combining ZrO_2 and CeO_2/ZrO_2 catalysts[12] and Pd/ZrO_2 catalyst[13]. Although the above mentioned processes could convert VA into valuable chemicals, high pressure hydrogen is required; this needs special hydrogen management and robust reactor design, which would account for a large portion of the working capital. Therefore, exploring alternative and sustainable strategies of VA (lignocellulose downstream) to value-added chemicals or biofuel (intermediates) is still necessary to supplement the current heterogeneous conversion processes.

The electrochemical approach is considered as a promising alternative that fulfils the principles of green chemistry [18-20]. Recently, synthetic organic electrochemistry has evoked the researcher's attention again [21,22]. More work has also been done on biomass conversion by electrochemical methods [23]. For example, furan compounds have been electrocatalytically converted into some fuel candidates such as 5-(hydroxymethyl)furfural (5-HMF), 2,5-dimethylfuran(DMF), 2-methylfuran(2-MF), 5-ethoxymethylfurfural (EMF), γ -valerolactone (GVL), ethyl levulinate and long chain hydrocarbon alkanes[24,25]. Levulinic acid could be electrochemically converted into valeric acid [11,26], γ -valerolactone[26,27], 2,7-octanedione[28], 4-hydroxy-2-butanone, 3-buten-2-one, and other fuels and chemicals like C8 platforms compounds[26,29]. Valeric acid could also be electrochemically oxidized to *n*-octane in water [26]. Santos *et al* [30] firstly investigated the electrochemical decarboxylation of oleic acid and triglycerides to olefin/ether mixtures on graphite plate electrode with the best Coulomb efficiency up to 50%. But the selectivity of methyl ether product was much lower (only 20%-40%) due to the strong deoxygenation performance of graphite plates electrode at high potential. Although many work have been done on electrocatalytic conversion of biomass-based compounds to valuable chemicals using the versatile electrodes like Pt, graphite, lead and so on, few work can achieve good selectivity for certain compounds or fuels. Therefore, highly selective electrocatalytic conversion of biomass to valuable fuels or chemicals is still a great challenge.

Recently, BDD electrode showed high potential to electrochemically oxidize MeOH to methoxy radicals in methanol solution [31]. This provided a possibility for electrochemical synthesis with high selectivity. Furthermore, as a promising alternative of clean renewable energy or additives for fuels, ether/ester chemicals have also attracted much attentions. Therefore, aiming to explore an

efficient and versatile electrocatalytic strategy to process biomass-derived feedstock, in this work, we developed a highly selective electrochemical method to product ether or ester chemicals using BDD electrode. The roles of supporting electrolytes, initial VA concentration, the initial VA/KOH ratio and the anodic potentials in the electrosynthesis were investigated. A rational mechanism for ethers formation on BDD in alcohols solution was proposed. To the best of our knowledge, this is the first time to achieve highly selective production of valuable ethers/esters from biomass-derived feedstock by electrochemical method.

2. EXPERIMENTAL SECTION

2.1 Material

Valeric acid (pentanoic acid, 99%, MACKLIN, China), potassium hydroxide (90%, Aladdin, American), sodium hydroxide (98%, Alfa Aesar GmbH & Co. KG, Germany), sodium perchlorate (99%, damas-beta, China), sodium methoxide in methanol (w=30%, Alfa Aesar GmbH & Co. KG, Germany), methanol (99.9%, Sigma-Aldrich, Germany), absolute ethanol (99.9%; Yuanli, China) were used as purchased. Dimethyl acetal (>98%, TCI, Japan), *sec*-butyl methyl ether (99%, Alfa Aesar GmbH & Co. KG, Germany), octane (>99%, MACKLIN, China), methyl valerate (98%, TCI, Japan) and valeric acid were used for GC and HPLC calibration curves. Here, dimethyl acetal is a homologue of 1,1-dimethoxybutane and 2,2-dimethoxybutane.

2.2 Electrocatalytic conversion of valeric acid

As shown in Fig. 1, all the experiments were conducted in a conventional three-electrode cells (15 ml) under potentiostatic control by an electrochemistry workstation (Princeton Applied Research, VersaSTAT MC, USA). Ag/AgNO₃ electrode (0.01 M AgNO₃ soluble in ACN, 0.799 V vs. SHE) was used as the reference electrode. A boron-doped diamond (BDD) and a platinum plate were used as the working electrode and the counter electrodes, respectively. Each electrode possessed a projected surface area of 5 cm². The distance between the working electrode and counter electrodes was 15 mm. Solutions of valeric acid in methanol or the mixture of methanol and ethanol were prepared and different supporting electrolytes (KOH, NaOH, NaClO₄ and CH₃ONa) were added to improve conductivity. Before the electrolysis, the cyclic voltammetry were performed from 1 V to 4 V at a scan rate of 50 mVs⁻¹ to obtain the onset potential. As shown in Fig. S1, the conductivity decreased as the addition of VA due to its suppression on the electrolyte dissociation[32]. The onset-potential for the oxidation of VA was about 2.0 V vs. Ag/Ag⁺. Therefore, the electrolysis was carried out at above 2.0 V vs. Ag/Ag⁺. The BDD electrode showed high activity and excellent stability for VA conversion (see Fig S2). At the end of experiment, all the electrodes were cleaned ultrasonically several times using water and ethanol solutions. Each experiment was repeated at least three times.

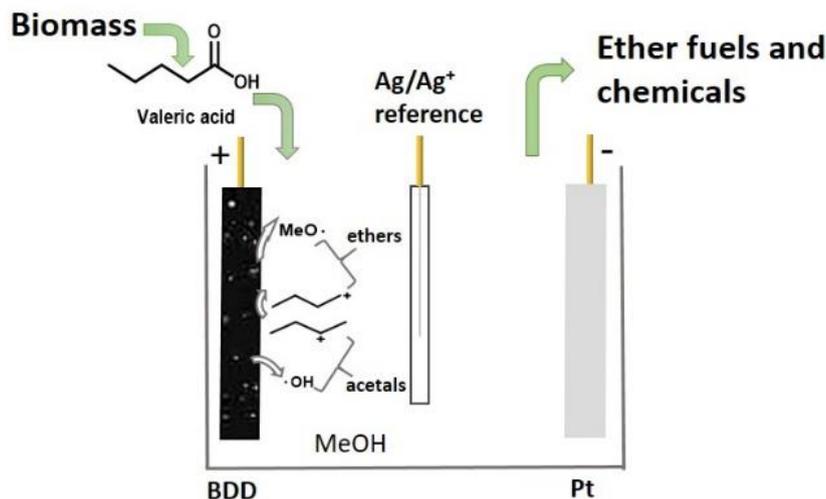


Figure 1. Schematic diagram of electrocatalytic conversion of VA on BDD electrode in methanol solution.

2.3 Products analysis

The products were analyzed qualitatively and quantitatively on an Agilent 7890N gas chromatography-5975N mass spectrometry (GC-MS, Agilent Technologies Inc, USA) equipped with a flame ionization detector (FID) and a HP5-5MS column (30m×0.25mm×0.25µm). The oven temperature was maintained at 60 °C for 8 min, then increased at 15 °C/min to 150 °C and held for 5 min, finally increased at 20 °C/min to 280 °C and held for 5 min. Helium was used as a carrier gas. The injector temperature was kept at 300 °C. The amount of unreacted valeric acid was quantitatively analyzed by high performance liquid chromatography (HPLC, Agilent Technologies Inc, USA) with a Kromasil C18 (250 mm×4.6 mm, S/N: 012304) column and a refractive index detector (RID). The gradient eluent of methanol and water was used as the mobile phase at a flow rate of 2 ml/min. The column temperature was maintained at 40 °C.

The conversion and selectivity were calculated according to Eq1 and Eq2.

$$\text{Conversion} = \frac{\text{mol}_{VA\text{-feed}} - \text{mol}_{VA\text{-product}}}{\text{mol}_{VA\text{-feed}}} \times 100\% \tag{1}$$

$$\text{Selectivity}_i = \frac{\text{mol}_{i\text{-product}}}{\sum \text{mol}_{i\text{-product}}} \times 100\% \tag{2}$$

Where $\text{mol}_{VA\text{-feed}}$ and $\text{mol}_{VA\text{-product}}$ are the mole amount of valeric acid in the feed and products, respectively, and $\text{mol}_{i\text{-product}}$ is the molar amount of different product.

Faraday efficiency was defined as Eq. (3):

$$\text{Faradaic efficiency} = \frac{\sum (\text{mol}_{i\text{-product}} \times n_{i\text{-product}}) \times F}{I \times t} \times 100\% \tag{3}$$

Where n is the number of electron transferred in the reactions to form products, F stands for the Faraday constant ($F = 96485 \text{ C mol}^{-1}$), I is the current observed in the experiment, and t is the reaction time.

3. RESULTS AND DISCUSSION

3.1 Selective conversion of VA on BDD in methanol

The electrocatalytic conversion of biomass-derived VA on BDD electrode in methanol was carried out in a single cell at 3.5 V. After 5 h electrolysis, ca. 41% of VA conversion was achieved and the products distribution are shown in Fig. 2. Obviously different from the products of olefin/ether mixtures over graphite anode at the potential of 5 V [30], the obtained products are dominated by two types of ethers, methyl ethers and methyl acetals, which constitute 83% of the products (42.8% for methyl ethers and 40.2% for methyl acetals). Moreover, the methyl ethers and methyl acetals are composed by two isomers, *n*- and *sec*-butyl methyl ether for methyl ethers and 1,1- and 2,2-dimethoxybutane for methyl acetals. Forwards, the selectivity toward *sec*-butyl methyl ether and 2,2-dimethoxybutane is about 1.5 times higher than their isomer, respectively. Meanwhile, some byproducts, methyl valerate (ester) and trace of octane in liquid and butane/butylene as well as carbon dioxide in gas products, are also produced, which is confirmed by GC-MS (Fig. S1&S3 and Table S1). And butylene is almost 9 times as much as butane. This result indicates that VA can be selectively converted into ethers by electrochemical approach using BDD electrode in methanol solution.

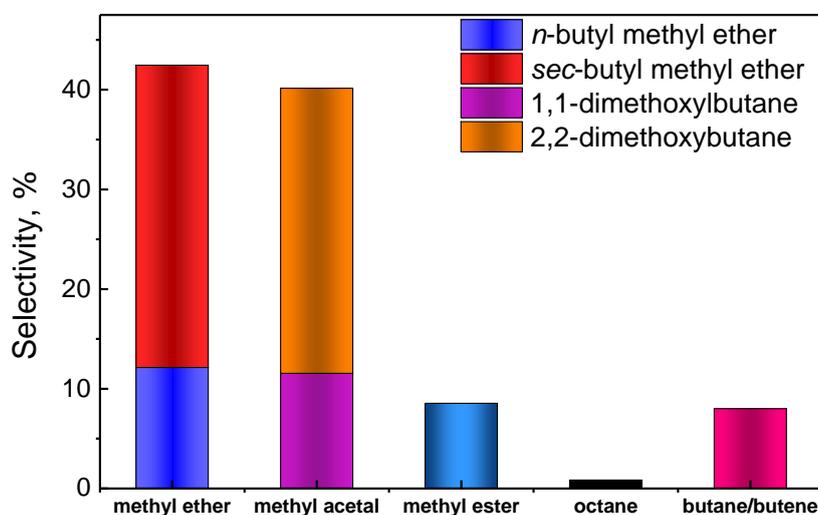


Figure 2. The products distribution of electrocatalytic conversion of VA in 0.5 M VA+ 0.3 M KOH methanol solution after 5 h electrolysis at 3.0 V under room temperature and ambient pressure.

3.1.1 Influence of supporting electrolytes

For the Kolbe reaction, current density is the most distinct parameter for the outcome [33,34]. Generally, the current density of the organic electrolyte could be enhanced by adding supporting electrolytes, but it will affect the selectivity and Faraday efficiency of the reactions, the pH, and potential secondary oxidant formation[35]. Therefore, different ion pairs such as KOH, NaOH, NaClO₄, and CH₃ONa as supporting electrolytes were investigated.

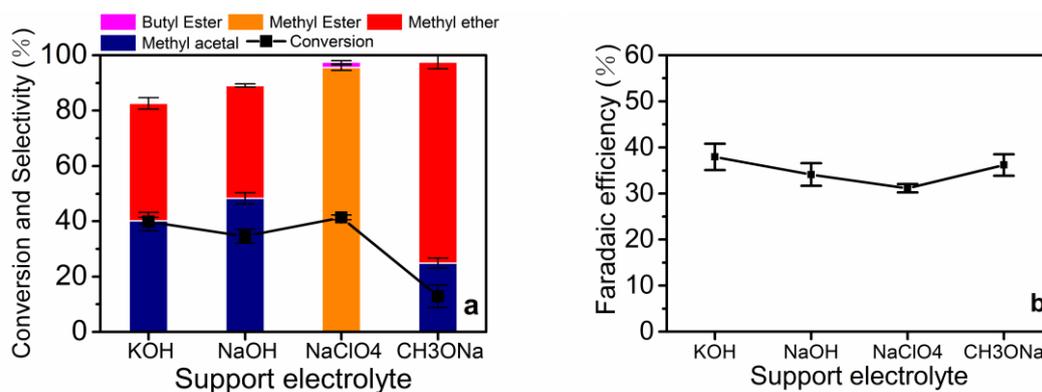


Figure 3. Effect of supporting electrolytes (fixed ion concentration: 0.3 M KOH, 0.3 M NaOH, 0.15 M NaClO₄, 0.15 M CH₃ONa) on selectivity of ethers and VA conversion (a) and Faraday efficiency for ether products (b) in electrochemical conversion of VA. Reactions were performed at 3.0 V for 5 h in the methanol solutions of 0.5 M VA under room temperature and ambient pressure.

Fig. 3a shows the dependence of products distribution and selectivity on the support electrolytes. It can be observed that the alkali metal cations and the counter ions have a significant effect on the VA conversion and the product selectivity. With KOH, NaOH and CH₃ONa as the supporting electrolytes, the products are dominated by methyl ether and methyl acetal. Comparing to KOH, NaOH as support electrolyte increased the selectivity of methyl acetal about 8% (up to 48.3%) but the selectivity of methyl ether is almost the same. This can be possible that the smaller alkali metal cation favors the reaction pathway for methyl acetal. Recently, CH₃ONa is considered a good catalyst for transesterification of fatty acids with methanol to produce biodiesel [36,37]. But with CH₃ONa as the supporting electrolyte, the liquid products almost only consist of methyl ether and methyl acetal (97.5% selectivity of ethers), and the selectivity of methyl ether is greatly enhanced (up to 72.6%). The selectivity of ethers is much higher than the results reported by Santos et al (20-35% selectivity toward ether) [30]. This can be speculated that the methoxy anion participates in formation of methyl ethers. Because methoxy anion can be transformed into methoxy radical (methoxy anion loses an electron to produce methoxy radical), which leads to the increase in methoxy radical concentration and ether selectivity [34]. Compared to cationic, the foreign anions may disturb the adsorption of the carboxylate ion on the anode, resulting in different reaction pathways. So it is found that the reaction pathway is thoroughly altered with NaClO₄ as the supporting electrolyte. This could be probably attributed to the acid system of electrolyte, which favors the transesterification of fatty acids with methanol[38]. The products contained 96.0% of the esters, which are dominated by methyl valerate and butyl valerate. While no ethers are detected. This indicates that esters can be highly selective produced in the same process just by tuning the type of supporting solution.

Recently, Stang et al [34] found that the conductivity is a key parameter to determine the current-voltage relationship of the electroorganic oxidation reactions. Increasing the supporting electrolyte concentration would increase total ion concentration to decrease the electrolyte resistance, thereby facilitating ion transport and enhancing the electrochemical reactions (like decarboxylation (Kolbe reaction), oxidation, et al.). So if the total ion concentration is the same, the conversion should

be similar. Therefore a close conversion of VA with KOH, NaOH and NaClO₄ as the supporting electrolytes is obtained. But with CH₃ONa as the support electrolyte, the conversion of VA reduces significantly. This can be attributed to the partial dissociation of CH₃ONa in methanol and high solution resistance derived from the low ions concentration due to the transformation of methoxyl anion into methoxyl radical. Though CH₃ONa increases the selectivity of methyl ether, but it decreases the conversion of VA obviously. In addition, KOH as supporting electrolyte shows higher Faraday efficiency than others, which is consistent with the literatures [29,30,39]. The Faraday efficiency for ether or ester products using different strong supporting electrolytes decreases slightly in the order: KOH>NaOH>NaClO₄. As for CH₃ONa, the Faraday efficiency increases slightly probably due to the increase of total ethers selectivity (Fig. 3b).

3.1.2 Effect of the initial molar ratio of VA to KOH

Basically, the solubility and acidity of fatty acids in alcohol solvent are very low, especially for the long-chain one[32, 40], and need to be improved by adding alkaline supporting electrolyte. Therefore, it is expected that the VA conversion would increase gradually with the increase of initial KOH addition (Fig. 4a). For low VA/KOH ratio feedstock, a quick increase in VA conversion to 27.9% (from 12.0% to 39.9%) is observed with the VA/KOH ratio from 5:1 to 5:3. But further increasing VA/KOH ratio up to 5:5, the VA conversion only increases ca. 6.7% (from 39.9% to 46.6%). In addition, the current density also increase as the VA/KOH ratio increase due to the enhancement of mass transfer (Table 1)[41]. These indicate that the formation of carboxylic acid ions from the neutralization between VA and KOH is restricted probably by an equilibrium between velarate and VA. Obviously, the products are dominated by methyl ether and methyl acetal with the molar ratio of VA to KOH not more than 5:5. Moreover, the selectivity of methyl ether is almost the same in this region. But the selectivity of methyl acetal decreased from 49.2% to 40.1% and then increased to 53.3%. The minimal methyl acetal selectivity was obtained at VA/KOH=5:3. Meanwhile the total selectivity of ethers is still higher than 80% and reached up to 95% at the VA/KOH ratio=5:5. All these can be attributed to the variation in reaction pathways.

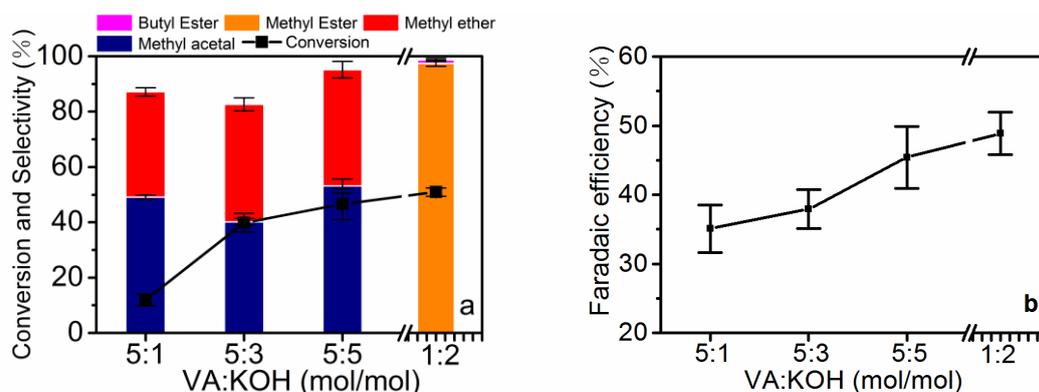


Figure 4. (a) The VA conversion and the selectivity of ethers and (b) Faraday efficiency for ether products in electrochemical conversion of VA on BDD electrode in methanol at different concentration of KOH. Reactions were performed potentiostatically at 3.0 V for 5 h in the methanol solutions of 0.5 M VA under room temperature and ambient pressure.

Interestingly, as excessive KOH (VA/KOH=1:2) was added, the products change suddenly into esters and the selectivity of these esters was almost 100%, no ethers are formed. This also proves directly that the initial molar ratio of VA to KOH has a profound influence on the selectivity of reaction pathways. On the other hand, owing to the reduction of solution resistance by adding KOH, the Faraday efficiency for ethers increased gradually up to 45.4% at the KOH/VA ratio=5:5 (Fig. 4b). For esters products, the Faraday efficiency further increased up to 48.9%. These results indicate that the better electrocatalytic performance (95% total selectivity) and Faraday efficiency (45.4%) can be achieved at the neutralization stoichiometric ratio (VA/KOH ratio at 5:5) for ether products, but strong alkaline favors the formation of esters.

Table 1. The effect of KOH concentration on pH value and current density.

Molar ratio of VA/KOH	5:1	5:3	5:5	1:2
pH value ^[a]	6.43	8.00	12.20	14.90
current density (mA cm ⁻²)	1.99-2.41	4.85-5.05	6.65-6.79	8.93-9.55

^[a] pH values were tested by METTLER TOLEDO pH meter

According to the literature, the neutral or weak acidity of the electrolyte and high current density prefer to carry out the Kolbe reaction, but non-Kolbe reaction occurs at low current density[32]. So the pH values and the current density were also monitored for different KOH addition. As shown in Table 1, the current density increases significantly with the addition of KOH, and the electrolyte gradually changes from an acidic system into strong alkaline one. There is a slight decrease in total selectivity as the pH value increases up to 8.0 (VA/KOH=5:3). The enhanced alkalinity by adding more KOH is beneficial to the electrochemical oxidation of VA (non-Kolbe reaction) to form methyl ether and methyl acetal. But the increased current density would enhance the decarboxylation of VA (Kolbe reactions) to produce butane, isobutene and octane (Fig. S3 and Table S1). Therefore, these two competing reactions are tuned due to the variation in pH value and current density by controlling the amount of KOH, resulting in the decrease of the total selectivity of ethers. Further increasing the pH value beyond 14 (VA/KOH=1:2), the reaction pathways is changed thoroughly to form esters.

3.2 Effect of feed concentration and anodic potential on ether products

As shown in Fig. 5a, the VA conversion decreased gradually from 65.0% to 15.2% with the VA feed concentration from 0.25 M up to 2.0 M, since the geometry of the electrode (full of active sites) involved in the catalytic process governs the electrochemical efficiency[27]. But the reaction rate accelerated to different content (Fig. 5b). This decline in conversion and the enhanced reaction rate is kinetically predictable. During the electrolysis, the reactant, VA, is firstly adsorbed on the active sites

on the electrode surface, and then transformed into radicals, which further form the final products. Therefore, the VA concentration would have a significant influence on this process[26,27,39].

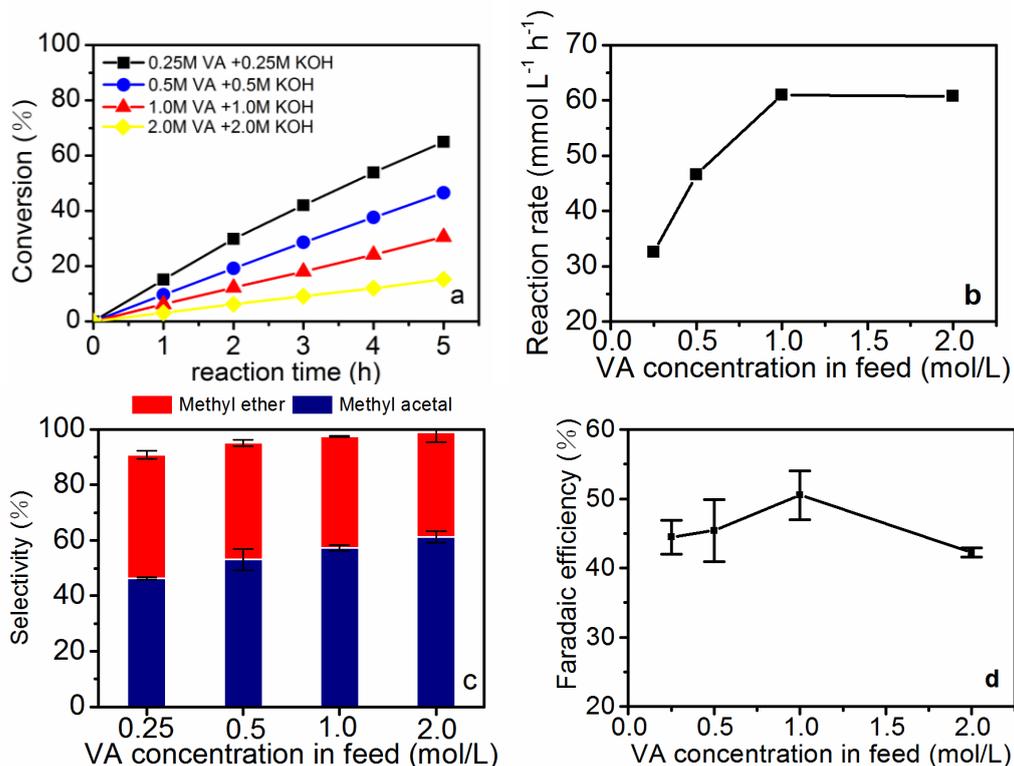


Figure 5. The VA conversion (a), reaction rate (b), selectivity of ethers (c) and Faraday efficiency (d) in electrochemical conversion of VA at various feed composition. Reactions were performed at 3.0 V for 5 h in the methanol solutions with VA:KOH=1:1 under room temperature and ambient pressure.

As shown in Fig. 5b, the reaction rate linearly increased with increasing VA feed concentration from 0.25 M to 1.0 M, and then keep constant as the VA feed concentration further increases up to 2.0 M. This suggests that at low VA concentration (≤ 1.0 M), the active sites on the electrode surface are unsaturated and the diffusion is the rate-determining step; but with the VA concentration beyond 1.0 M, the active sites become saturated and the rate-determining step switches to the electrochemical conversion of VA on the electrode surface.

Due to the presence of more supporting electrolyte (KOH), the current density increases and the electrochemical oxidation reactions are enhanced because that sufficiently high concentration of strong electrolyte has a positive impact to the selectivity and Coulombic efficiency[26,28,39]. As shown in Fig. 5c, the selectivity of ether products is higher than 90% for different VA feed concentrations, and gradually increase with the feed concentration increasing. At 2.0 M, the selectivity of ethers was nearly 99%. But Faraday efficiency reached a maximum value at 1.0 M VA (50.5%) followed by a sharp decline at 2.0 M (Fig. 5d), probably due to the transfer of the rate-determining steps. The enhancements of selectivity and faraday efficiency may be attributed to the increased current density and reduced resistance of the electrolyte. These results were further confirmed by the

experiments with the molar ratio of VA to KOH at 5:3 under the same conditions (Fig. S4). The similar variation trend for the conversion, reaction rate and Faraday efficiency was also observed. These indicate that for the electrocatalytic conversion of VA on BDD electrode, the VA feed concentration of 1.0 M seems to be a critical one and the optimum reaction rate and faraday efficiency are achieved at this concentration for ether products.

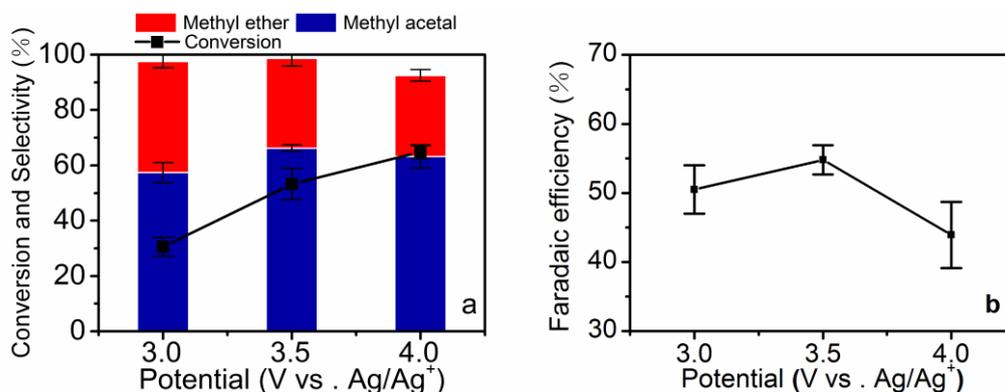


Figure 6. (a) The VA conversion and selectivity of ether and (b) Faraday efficiency for electrochemical conversion of VA in methanol under different anodic potentials. Reaction was carried out for 5 h in 1.0 M VA+1.0 M KOH methanol at room temperature and ambient pressure.

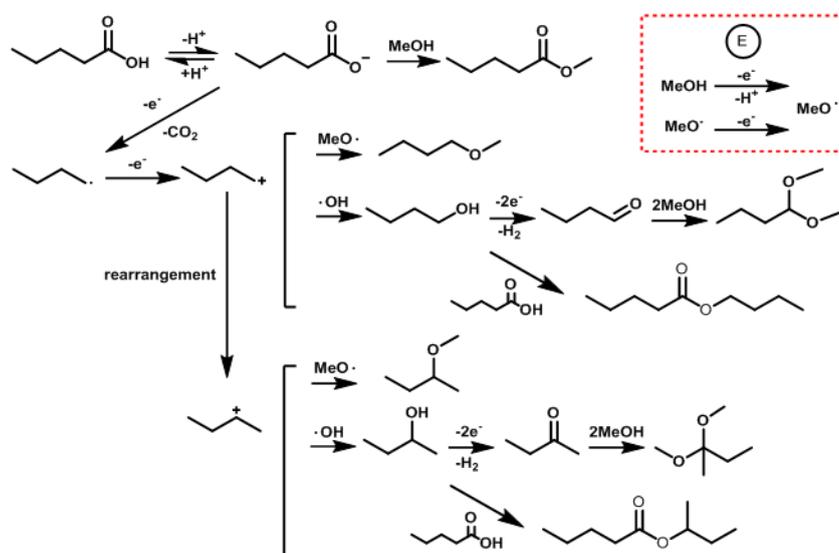
The applied potential is also one of the important parameters for efficient electrolysis. The unwanted side reaction would become more competitive under more deviant potential from the onset ones[11], which resulted in lower selectivity of target products and Faraday efficiency (FE). For many electrochemical reactions or electrolysis, a maximum Faraday efficiency (FE) is expected by suppressing the side reactions [11,42-45]. Fig. 6 shows the influence of anodic potentials on the electrocatalytic VA conversion. With the increase in the anodic potentials, the conversion of VA gradually increased. At 4.0 V, the conversion of valeric acid was almost up to 65% after 5 h. It could be found that the main products are still methyl ether and methyl acetal. As the potential increasing from 3.0 V to 3.5 V, the total selectivity of ether products increased from 97.5% to the maximum value 98.7% (with 53.3% conversion of VA). Interestingly, the selectivity of methyl ether decreased slightly (from 40.1% to 32.5%), but the selectivity of methyl acetal significantly increased from 57.4% to 66.2%. This trend indicates that the formation mechanisms for these two products on the BDD surface are different. On BDD electrode high potential is more likely to produce hydroxyl radical than methoxy radical, which results in the selectivity decrease of methyl ether[35]. But further increasing the anodic potential to 4.0 V, the total selectivity of products slightly decreased, in which the selectivity toward methyl ether and acetals decreased simultaneously.

Apparently, high potential can also enhance the Kolbe reaction to generate the gaseous by-products, resulting in the decrease of total selectivity of ether products[46]. The gas products were monitored and analyzed by GC-MS. As mentioned above, only butane, butene and carbon dioxide were detected in the gas products. As the potential increasing from 3.5 V to 4.0 V, more gas products were obtained, further confirming the enhancement of decarboxylation (Kolbe reaction). Comparing to

platinum and graphite electrodes reported in literature[26,30], BDD electrode shows high selectivity for ether products (> 90%). In this regard, the variation in Faraday efficiency at different potential could be easily comprehended. As shown in Fig. 6b, Faraday efficiency reached a maximum value (ca.58%) at 3.5 V. Meanwhile, more positive potential could not further improve the conversion except for power consumption. Therefore, the optimum selectivity and Faraday efficiency (FE) was achieved at an anodic potential of 3.5 V vs. Ag/Ag⁺.

3.3 Possible reaction mechanism of valeric acid to ethers/esters on BDD electrode

Kolbe reaction and non-Kolbe reaction have been widely studied, but with the new theory and technology, this ancient reaction can be expanded and promote the fundamental research in the field of electrochemistry. According to the references, fatty acids can be decarboxylated at the anode to form a radical, and then oxidized to a carbocation through a non-Kolbe reaction, leading to the formation of ether, ester, alcohol and other products on different electrodes[47,48]. Dos Santos et al reported that the electrochemical decarboxylation of oleic acid would lead to the binary products of olefin/ether mixtures in methanol solution on graphite plate electrodes[30]. BDD electrode is known to generate hydroxyl radical and other active intermediates directly on the electrode surface[40]. Dolson and Swenton reported that methoxy radicals are generated in electrochemical oxidation of MeOH on BDD anode, which was supported by the ESR spectroscopic data[31]. In this work, valeric acid was converted into ethers and esters on BDD electrodes in methanol with high selectivity. Except the byproducts of gaseous hydrocarbons during the electrolysis, it is found that there always presents the products of butanol and sec-butyl alcohol in the interval samples for ether products(See the GC-MS results in Fig. S1 and Table S1). This indicates that these two isomeric alcohols should be the intermediates for the formation of methyl acetals. Based on these results, a possible electrochemical reaction mechanism can be proposed as Scheme 1.



Scheme 1. Proposed reaction pathways of electrocatalytic conversion of valeric acid on BDD electrode in methanol.

Stang et al [34] reported that the decarboxylation of the carboxylic acid would take place through a one-electron oxidation at the anode, leading to the formation of an alkyl-radical. Then the alky-radicals are easily inclined to undergo a second oxidation to yield carbocation ion that further react to non-Kolbe products[34,35,47]. Sumi et al [31] demonstrated that BDD anode favored the methanol to generate methoxy radicals and showed higher selectivity of anodic oxidation of isoeugenol to produce (\pm)-licarin A than Pt and GC electrodes. So it could be speculated that VA is firstly dihydrogen to produce the valerate and then decarboxylated to form butyl radical. The formed valerate combined with methanol to form methyl valerate. And then the butyl radical is oxidized to the carbocation ion. But the carbocation ions are prone to rearrange[47] and can combine with hydroxyl radical and methoxy radical generating from water formed and the solvent methanol on BDD electrode[35,40,49]. The carbocation ions bond with the methoxy radical to form methyl ethers (*n*-butyl methyl ether and the isomer *sec*-butyl methyl ether), in which the methoxy radicals are formed by anodic oxidation of MeOH followed by chemical reaction of the derived radical and ionic species (see Scheme 1) [35]. Meanwhile, the carbocation ions reacting with hydroxyl radical would generate the products of butanol and *sec*-butyl alcohol. Then the formed alcohols would be oxidized to aldehydes or ketones, which are detected by GC-MS and also reported by Stang et al [34]. These aldehyde/ketones would react with methanol via Aldol reaction to form the final product methyl acetals. Unfortunately, due to the high reaction rate of the intermediates, it is difficult to obtain the tendency of the intermediates concentration[40]. Moreover, hemiacetals are instable and would further react with methanol, therefore only acetals are detected in the final products. In addition, it is found that the selectivity of 2,2-dimethoxybutane (from ketone) is higher than that of 1,1-dimethoxybutane (from aldehyde) in all the products. Meanwhile, the selectivity of *sec*-butyl methyl ether is higher than *n*-butyl methyl ether. These suggest that the rearrangement of carbocation ion is more favorable under the experimental conditions. In addition, the carbocation ions also could react with valerate to form butyl valerate, which was also determined by GC-MS. According to this mechanism, the other α -alkoxys as the solvent would show the similar performance in this electrochemical process. The products distribution in ethanol solution in Fig S6 also verify this speculation.

4. CONCLUSIONS

This work demonstrated an efficient electrochemical method to convert valeric acid into ethers and esters products. BDD is a promising anode to carry out this process. The reaction pathways (for ether or ester products) and Faraday efficiency can be tailored by tuning the supporting electrolytes, initial VA/KOH ratio, feed concentration and anodic potentials. The supporting electrolytes, the pH value (initial molar ratio of VA to KOH), anodic potential and feed concentration show significant effect on the electrocatalytic conversion of VA to ethers products. The VA feed concentration can affect the rate-determining steps in the electrocatalytic conversion of VA, and 1.0 M is the critical feed concentration for the reaction rate and energy efficiency. NaClO₄ as supporting electrolyte and

excessive alkaline will alter the reaction pathways to produce esters with high selectivity. Relative high anodic potential can enhance the selectivity of ethers, especially for the acetals. The optimum selectivity of total ether products, up to 98.7% with good conversion and faraday efficiency, are achieved with VA/KOH=1:1 at 3.5 V vs. Ag/Ag. The rational electrocatalytic mechanism of ether formation on BDD electrode is developed. The rearrangement of carbocation ion is more favorable under the experimental conditions. Methyl radical is easier to generate than the ethyl radical on BDD electrode. This method could also be expanded to obtain long-chain ether and acetal in different α -alcohol solution, eg. ethyl ether and ethyl acetal. In addition, the BDD electrode showed much higher activity and selectivity for etherification of fatty acid with methanol.

ACKNOWLEDGEMENTS

The financial support by National Natural Science Foundation of China (Grant No. 21476169) is gratefully acknowledged.

References

1. R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba, M. López Granados, *Energy. Environ. Sci.*, 9 (2016) 1144.
2. L. Hu, G. Zhao, W. Hao, X. Tang, Y. Sun, L. Lin, S. Liu, *RSC Adv.*, 2 (2012) 11184.
3. A. Bohre, S. Dutta, B. Saha, M. M. Abu-Omar, *ACS Sustain. Chem. Eng.*, 3 (2015) 1263.
4. D. Klein-Marcuschamer, H. W. Blanch, *AIChE J.*, 61 (2015) 2689.
5. A. Demirbas, *Prog. Energy Combust. Sci.*, 33 (2007) 1.
6. K. Kulyk, B. Palianytsia, J.D. Alexander, L. Azizova, M. Borysenko, M. Kartel, M. Larsson, T. Kulik, *ChemPhysChem.*, 18 (2017) 1943.
7. I. L. Simakova, D. Y. Murzin, *Energy Chem.*, 25 (2016) 206.
8. J. P. Lange, R. Price, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosselink, *Angew. Chem., Int. Ed.*, 49 (2010) 4479.
9. K. Kon, W. Onodera, K. Shimizu, *Catal. Sci. Technol.*, 4 (2014) 3227.
10. L. L. Dong, L. He, G. H. Tao, C. Hu, *RSC Adv.*, 3 (2013) 4806.
11. L. Xin, Z. Zhang, J. Qi, D. J. Chadderton, Y. Qiu, K. M. Warsko, W. Li, *ChemSusChem*, 6 (2013) 674.
12. Y. A. Zaytseva, V. N. Panchenko, M. N. Simonov, A. A. Shutilov, G. A. Zenkovets, M. Renz, I. L. Simakova, V. N. Parmon, *Top. Catal.*, 56 (2013) 846.
13. M.N. Simonov, Y.A. Gulaeva, I.P. Prosvirin, I.A. Chetyrin, I.L. Simakova, *J. Sib. Fed. Univ.: Chem.*, 6 (2013) 331.
14. J. C. Serrano-Ruiz, D. J. Braden, R. M. West, J. A. Dumesic, *Appl. Catal. B: Environ.*, 100 (2010) 184.
15. J. C. Serranoruiz, D. Wang, J. A. Dumesic, *Green Chem.*, 12 (2010) 574.
16. M. Gliński, J. Kijęński, *React. Kinet. Catal. Lett.*, 69 (2000) 123.
17. A. Corma, B. Oliver-Tomas, M. Renz, I. L. Simakova, *J. Mol. Catal. A: Chem.*, 116 (2014) 388.
18. R. Francke, R. D. Little, *Chem. Soc. Rev.*, 43(2014) 2492.
19. S. R. Waldvogel, B. Janza, *Angew Chem., Int. Ed.*, 53 (2014) 7122.
20. H. J. Schäfer, *C. R. Chim.*, 14 (2011) 745.
21. M Yan, Y Kawamata, *P S. Baran, Chem. Rev.*, 117 (2017) 13230.
22. Y Jiang, K Xu, C Zeng, *Chem Rev*, Article ASAP, DOI: 10.1021/acs.chemrev.7b00271
23. O. O. James, W. Sauter, U. Schroder, *ChemSusChem*, 10 (2017) 2015.
24. P. Nilges, U. Schröder, *Energy. Environ. Sci.*, 6 (2013) 2925.

25. Y. Kwon, K. J. P. Schouten, J. C. van der Waal, E. de Jong, M. T. M. Koper, *ACS Catal.*, 6 (2016) 6704.
26. P. Nilges, T. R. dos Santos, F. Harnisch, U. Schröder, *Energy Environ. Sci.*, 5 (2012) 5231.
27. Y. Qiu, L. Xin, D. J. Chadderdon, J. Qi, C. Liang, W. Li, *Green Chem.*, 16 (2014) 1305.
28. T. R. dos Santos, P. Nilges, W. Sauter, F. Harnisch, U. Schröder, *RSC Adv.*, 5 (2015) 26634.
29. J. R. Sherwood, *ChemSusChem*, 10 (2017) 166.
30. T. R. dos Santos, F. Harnisch, P. Nilges, U. Schroder, *ChemSusChem*, 8 (2015) 886.
31. T. Sumi, T. Saitoh, K. Natsui, T. Yamamoto, M. Atobe, Y. Einaga, S. Nishiyama, *Angew Chem., Int. Ed.*, 51 (2012) 5443.
32. Zoski, G. Cynthia, *Handbook of Electrochemistry*, Elsevier, (2007).
33. B. Speiser, *Methods to Investigate Mechanisms of Electroorganic Reactions*, Wiley-VCH Verlag GmbH & Co. KGaA, (2007).
34. C. Stang, F. Harnisch, *ChemSusChem*, 9 (2015) 50.
35. M. G. Dolson, J. S. Swenton, *J. Am. Chem. Soc.*, 103 (2002) 2361.
36. D. Zeng, L. Yang, T. Fang, *Fuel*, 203 (2017) 739.
37. Y.C. Sharma, B. Singh, D. Madhu, Y. Liu, Z. Yaakob, *Biofuel Res. J.*, 1(2014) 78.
38. I. B. Banković-Ilić, O. S. Stamenković, V. B. Veljković, *Renew. Sust. Energ. Rev.*, 16 (2012) 3621.
39. C. Urban, J. Xu, H. Sträuber, T. R. dos Santos Dantas, J. Mühlberg, C. Härtig, L. T. Angenent, F. Harnisch, *Energy Environ. Sci.*, 10 (2017) 2231.
40. G. S. Pande, S. N. Shukla, *Electrochim. Acta*, 4 (1961) 215.
41. M.T. Hicks, P.S. Fedkiw, *J. Electroanal. Chem.*, 424 (1997) 75.
42. J. J. Roylance, T. W. Kim, K.-S. Choi, *ACS Catal.*, 6 (2016) 1840.
43. J. J. Roylance, K.S. Choi, *Green Chem.*, 18 (2016) 2956.
44. J. J. Roylance, K.S. Choi, *Green Chem.*, 18 (2016) 5412.
45. D. J. Chadderdon, L. Xin, J. Qi, Y. Qiu, P. Krishna, K. L. More, W. Li, *Green Chem.*, 16 (2014) 3778.
46. V. N. Andreev, V. I. Bykov, V. A. Grinberg, A. G. Dedov, A. S. Loktev, N. A. Mayorova, I. I. Moiseev, A. A. Stepanov, *Russ. J. Electrochem.*, 49 (2013) 216.
47. H. J. Schäfer, *Eur. J. Lipid Sci. Technol.*, 114 (2012) 2.
48. P. F. Levy, J. E. Sanderson, R. G. Kispert, D. L. Wise, *Enzyme Microb. Technol.*, 3 (1981) 207.
49. H. J. Schäfer, *Recent contributions of kolbe electrolysis to organic synthesis*, Springer (1990) Berlin Heidelberg.