Short communication

Sub/supercritical carbon dioxide induced phase switching for the reaction and separation in ILs/methanol

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Abstract

Separation of products from ionic liquid (IL) solvents is one of the main challenges that hinder their utilizations. In this study, the production of γ-valerolactone (GVL) by selective hydrogenation of α-angelica lactone (AL) and separation of the products from the IL solvent were carried out by using subcritical CO2 as a “switch” at room temperature. After the mixture was separated into two phases by subcritical CO2, AL and nano Pd/C catalyst were only found in the lower IL-rich phase, GVL was produced with quantitative yield and enriched in the upper methanol-rich phase. Pure GVL can be obtained by depressurizing to release CO2 and evaporation to remove methanol of the upper phase, the lower phase containing IL, catalyst and methanol can be recycled for the next reaction. The strategy may provide a new approach to produce and separate products from IL solvents at mild conditions.

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Keywords: Separation; Ionic liquids; Selective hydrogenation; Mild condition; Subcritical CO2

1. Introduction

The major biomass components, cellulose and hemicelluloses, can be converted into various chemicals and fuels including sugars, ethanol, butanol, ethylene glycol, 5-(Hydroxymethyl)furfural, dimethylfuran and so on [1–10]. Among these biomass derived chemicals, γ-valerolactone (GVL) was paid special attention [11–14]. Horvath et al. [15] demonstrated that the biomass-derived compound γ-valerolactone can be used as solvent and fuel additives due to its several very attractive physical and chemical properties. GVL also can be converted into valuable chemicals including 1,4-pentanediols, dimethyl adipate, methyl pentenoate, 2-MeTHF, butene, pentenoic acid and so on [16]. Recently, Dumesci et al. introduced a strategy to produce soluble carbohydrates from corn stover, hardwood and softwood at high yields (70–90%) with the aid of GVL by promoting thermocatalytic saccharification through complete solubilization of the biomass, even including the lignin fraction [17]. In our previous studies, we also converted GVL into high octane number gasoline [18]. However, the industrial production of GVL has not been realized due to high cost and harsh reaction conditions.

There are several pathways to produce GVL, hydrogenation of levulinic acid (LA) to γ-hydroxyvaleric acid and followed by ring-closing and dehydration, hydrogenation of levulinate to make the hydroxy levulinic ester and further intramolecular transesterification [12,19–21]. For example, LA/water solution with a yield higher than 95% was obtained with Ru(a-acac)3/TPPTS catalyst at 140 °C and 10 MPa for 12 h [20]. Tang et al. reported a green and efficient method for the conversion of ethyl levulinate into GVL by supercritical ethanol as the hydrogen donor and a good GVL yield of 82% was achieved at 250 °C [22]. Recently, many types of efficient...
catalysts were developed for the hydrogenation reaction [23–31]. Although these pathways are well-established and their conversions and yields are attractive, effective reduction of LA at mild conditions is proven to be difficult. We developed an efficient route for the production of GVL by hydrogenation of $\alpha$-angelica lactone (AL) that can be produced by dehydration of LA with solid acid catalyst with high yield using a series of room-temperature ionic liquids (ILs) as the reaction solvents at room temperature [32–34]. Furthermore, the reaction system of IL/catalyst showed a good reusability, there was no decrease in conversion and selectivity after 10 cycles [34].

However, the commonly employed approaches for the separation of the final products from the ILs solvents are still difficult. Since most ILs are non-volatile [35–37], evaporation or distillation of the other components in the ILs is a feasible option, but evaporation and distillation are not practical for high-boiling or thermally unstable compounds and they also consume a lot of energy [38]. The other choice for the separation is extraction, but extraction by other organic solvents may cause cross contaminations between extractors and products and deteriorate the reusability of the catalysts and the solvents. Followed by the pioneer work by Brennecke et al. [38–43], many reactions were carried out by employing ILs and supercritical CO2 systems, which achieved either high selectivity or efficient separations by supercritical CO2 extraction [44–54]. Due to the non-polar of supercritical CO2, it is not able to dissolve compounds with high polarity like GVL. Herein, we report a highly efficient catalytic system for the hydrogenation and separation in a biphasic system employing sub/supercritical CO2 as a phase separation “switch”, in which, both reaction and separation can be carried out in the same system operated in batch type or continuous type at room temperature. As shown in Fig. 1, the hydrogenation of AL to GVL can be carried out in 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF6)/methanol solution at room temperature catalyzed by nano Pd/C catalyst (Fig. 1a). After the reaction, CO2 is introduced to form an Al solution at room temperature catalyzed by nano Pd/C catalyst also only needed with stirring to avoid settling of the catalyst. When the reaction was completed, upper and lower phases were sampled to designed pressure. The inlet value was closed and heated if needed with stirring to avoid settling of the catalyst. When the reaction was completed, upper and lower phases were sampled by a 1 ml sampler, CO2 and H2 were slowly released and weight of CO2 was calculated by weight lose, the liquid compositions were analyzed by HPLC, Due to the low solubility of H2 in both methanol and IL, composition of H2 was not counted.

The products were analyzed by HPLC (Agilent 1100) equipped with a refractive index (RID) detector and an ODS-BP column (0.46 × 250 mm). Acetonitrile and water with a ratio of 3:7 was used as the mobile phase. The mobile phase was sonicated for 30 min before use. The oven temperature were set at 40 °C with a flow rate of 0.8 ml/min.

3. Results and discussion

Methanol and BmimPF6 are completely miscible in any proportions at room temperature [55]. We firstly carried out
the hydrogenation of AL to GVL in BmimPF6/methanol with nano Pd/C as the catalyst at low temperature. As shown in Fig. 2, the reaction rate is rather fast even at room temperature; fully conversions of AL are achieved with 20 min and 30 min at 40 °C and room temperature respectively. It is found that the reaction rate is higher compared with our previous study [34]. The main reason is that the viscosity of BmimPF6 is higher than that of methanol [56,57], the addition of methanol prompts the mass transfer.

After the reaction was completed, CO2 was pumped to induce a separation of the mixture of BmimPF6 + methanol + GVL + AL + CO2 + catalyst system. As we expected, the mixture formed a biphasic system at pressure higher than 6.0 MPa (Table 1). For all pressures, there was no detectable BmimPF6 in the upper phase, indicating that the solubility of BmimPF6 in the upper phase is lower than the determination limit of HPLC, which is similar to that reported before [55]. This is not surprising because the solubility of the IL in CO2 is extremely low [58,59] and the methanol in the upper phase did not increase the solubility of IL in methanol + CO2. In another word, the methanol in the upper phase cannot improve the solvent power of the CO2 and it is further concluded that the upper phase contains only GVL, methanol and CO2. Many researches proved that there are strong interactions between CO2 and ILs that results in high CO2

Table 1
Composition (mol%) of upper phase and lower phase induced by CO2 at various pressures.α,β

<table>
<thead>
<tr>
<th>CO2/Mpa</th>
<th>XGVL</th>
<th>XMeoh</th>
<th>XILs</th>
<th>XCO2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Upper</td>
<td>Lower</td>
<td>Upper</td>
<td>Lower</td>
</tr>
<tr>
<td>6.0</td>
<td>0.0451</td>
<td>0.0590</td>
<td>0.1891</td>
<td>0.0370</td>
</tr>
<tr>
<td>8.0</td>
<td>0.0392</td>
<td>0.0522</td>
<td>0.1584</td>
<td>0.0396</td>
</tr>
<tr>
<td>10.0</td>
<td>0.0265</td>
<td>0.0482</td>
<td>0.1305</td>
<td>0.0903</td>
</tr>
<tr>
<td>12.1</td>
<td>0.0250</td>
<td>0.0189</td>
<td>0.1694</td>
<td>0.0335</td>
</tr>
</tbody>
</table>

α Conditions: 25 °C, standing for 2 h, 2.0 g GVL (0.02 mol), 5.0 g (0.0176 mol) BmimPF6, 8.7 g (0.275 mol) methanol, 10% Pd/C: 0.06 g (3 wt% of AL).

β See Table S2 for composition in wt%.

Fig. 2. Selective hydrogenation of AL to GVL at 25 °C and 40 °C. Reaction conditions: 4.0 MPa H2, 2.0 g (0.02 mol) α-AL, 5.0 g (0.0176 mol) BmimPF6, 8.7 g (0.275 mol) methanol, 10% Pd/C: 0.06 g (3 wt% of AL).
solubility in BmimPF$_6$ [59], but CO$_2$ is non-polar and not capable of dissolving BmimPF$_6$ [60]. Conversely, methanol is high polar, protic and possesses the ability to solvate ions. As CO$_2$ is dissolved in the upper phase, the solution expands substantially and the mixture of methanol/CO$_2$ is no longer a good solvent for BmimPF$_6$. Due to the gaseous nature of CO$_2$ and low boiling point of methanol under atmospheric pressure, pure GVL can be obtained by simply release the pressure and evaporation of methanol from the upper phase. If evaporation of methanol is carried out under negative pressure, the temperature employed can be as low as room temperature. The low separation temperature is extremely useful for the thermally unstable compounds and the bioactive organic compounds [61,62].

It is also seen from Table 1 that the fraction of CO$_2$ in the lower phase increased with the increase of pressure while that in the upper phase did change greatly. Both fractions of GVL in the upper phase and the lower phase decreased with the increase of pressure. However, the fraction ratio of GVL in the upper phase and the lower phase was 0.76 at 6.0 MPa, which increased to 1.32 at 12.1 MPa, indicating that partition coefficient was improved at higher CO$_2$ pressure. As we mentioned before that GLV is polar and CO$_2$ is non-polar, the increase of CO$_2$ fraction in BmimPF$_6$ at high pressure makes the GLV moving to the upper phase containing much methanol with high polarity, thus leads to higher partition coefficient.

In-situ reaction and separation also can be carried out simultaneously as shown in Fig. 1c. Before the reaction, 2.082 g (0.021 mol) AL, 5.0 g BmimPF$_6$ (0.0176 mol), 8.7 g (0.275 mol) methanol and 0.06 g 10% Pd/C catalyst were mixed and subjected into the reactor, 6.0 MPa of CO$_2$ was pumped to form a biphasic system and stabilized for 30 min. Then 4 MPa H$_2$ was pumped to start the selective hydrogenation. AL and GLV distributed in the upper phase containing IL, catalyst and methanol can be recycled for the next reaction. In the in-situ reaction and separation process, the AL in the lower phase is continuously hydrogenated into GVL and extracted to the upper phase. The research provides a new method to carry out the reaction and separate the products, catalysts and IL solvents without using solvent extraction, evaporation that may contaminate or deteriorate the product or reaction solvent.

We also studied the effects of CO$_2$ and H$_2$ pressures on the conversion of AL and the results are summarized in Table 3. At constant H$_2$ pressure (Entry 1–4, Table 3), the increase of CO$_2$ pressure from 2.4 MPa to 4.0 MPa changed the mixture from one-phase to two-phase. However, the increase of CO$_2$ pressure decreased the conversion of AL possibility due to that much CO$_2$ added diluted the concentration of AL and the catalyst. On the contrary, at constant CO$_2$ pressure (Entry 5–8, Table 3), the increase of H$_2$ pressure changed the mixture from two-phase to one-phase, indicating that high H$_2$ pressure prevents the formation of biphasic system. The simple explanation for our observations is that the solubility of CO$_2$ in the methanol/IL mixture is highly correlated with the pressure [39,43,58]. The solubility of CO$_2$ in BmimPF$_6$ is 0.27 g/g at 4 MPa and 40 °C, while the solubility increases 2 times to 0.57 g/g at 10 MPa [63]. When H$_2$ was introduced into the reactor, the total pressure was subsequently increased; much CO$_2$ in the upper phase was transferred and dissolved in the lower phase. Therefore the biphasic system integrated to single phase system. Regardless the phase behavior, high H$_2$ pressure is favored for the selective hydrogenation, a H$_2$ pressure of 2.0 MPa gave a conversion of 15% (entry 5, Table 3), the value increased to 69% when H$_2$ pressure was increased to 8.2 MPa (entry 8, Table 3).

### Table 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>P$_{\text{CO}_2}$ (MPa)</th>
<th>P$_{\text{H}_2}$ (MPa)</th>
<th>Conversion (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>4.2</td>
<td>2.4</td>
<td>73</td>
</tr>
<tr>
<td>2</td>
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<td>4.0</td>
<td>65</td>
</tr>
<tr>
<td>3</td>
<td>4.2</td>
<td>6.0</td>
<td>62</td>
</tr>
<tr>
<td>4</td>
<td>4.2</td>
<td>7.9</td>
<td>58</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
<td>4.0</td>
<td>58</td>
</tr>
<tr>
<td>6</td>
<td>4.2</td>
<td>4.3</td>
<td>44</td>
</tr>
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</tr>
<tr>
<td>8</td>
<td>8.2</td>
<td>4.0</td>
<td>69</td>
</tr>
</tbody>
</table>

*Conditions: 2.082 g (0.021 mol) AL, 5.0 g BmimPF$_6$ (0.0176 mol), 8.7 g (0.275 mol) methanol and 0.06 g 10% Pd/C, 25 °C, 6.0 MPa CO$_2$ for 0.5 h and then 4.0 MPa H$_2$ was pumped.*
Conflict of interests

The authors declare no conflict of interests.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.gee.2016.04.002

References