ACS Sustainable Chemistry & Engineering
Research Article
pubs.acs.org/journal/ascecg

Efficient Conversion of α-Angelica Lactone into γ-Valerolactone with Ionic Liquids at Room Temperature

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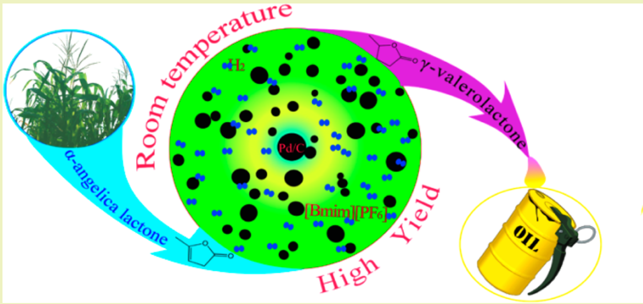
Supporting Information

ABSTRACT: γ-Valerolactone, which can be produced from lignocellulosic biomass, has drawn increasing attention recently because of its benign properties and versatile functions. However, the temperature employed for its production is relatively high. In order to save energy, herein, a new transformation process of α-angelica lactone to γ-valerolactone was carried out by using a series of room-temperature ionic liquids as solvents in a batch-type reactor. Among these ionic liquids, [Bmim]PF_6 showed the best performance on the selective hydrogenation at 60 °C with a reaction time of 20 min. Interestingly, it was found that the reaction can also take place at a temperature as low as room temperature with complete conversion and nearly 100% selectivity, which greatly reduces the energy required for the production of γ-valerolactone. The reaction system of ionic liquid/catalyst showed good reusability. There was no obvious decrease in conversion and selectivity after 10 uses. Furthermore, the kinetics of the catalytic hydrogenation reaction of α-angelica lactone was studied to elucidate the reaction profile. Systematic kinetics experiments were carried out by varying the reaction temperature from 20 to 100 °C at 4.0 MPa, and the simulated data fits well with the first-order reaction law.



KEYWORDS: *α-Angelica lactone, γ-Valerolactone, Ionic liquids, Hydrogenation, Kinetics*

INTRODUCTION

With the supply of nonrenewable fossil fuel diminishing, more attention has been paid to the conversion of renewable feed stocks into chemicals and biofuels.[1,2] In this aspect, γ-valerolactone (GVL), which can be produced from lignocellulosic biomass, has drawn increasing attention because of its benign properties and versatile functions in recent years.[3−5] GVL occurs naturally in fruits such as peaches and coconuts and has been used in the food industry. Meanwhile, numerous unique physical and chemical properties of GVL have made it an ideal liquid for use as solvent, fuel additive, perfume, and intermediate in the synthesis of many fine chemicals.[6−9] Therefore, GVL has been identified as a promising, sustainable platform molecule for next-generation biorefineries.[10] There are numerous reports on the synthesis of carbon-based chemicals with GVL, such as 1,4-pentanediols,[11,12] mixtures of alkanes and 2-methyl-tetrahydrofuran,[11] butenes,[13] 4-hydroxypen-tanamides,[14] methyl-pentanoate,[15] and adipic acid via pentenoic acids.[16−18] Moreover, in order to produce GVL from biomass, different approaches have been discovered by several groups. The starting materials for obtaining GVL are always levulinic acid (LA) and its esters. Some researchers investigated the hydrogenation of LA with external hydrogen or in situ hydrogen decomposed from formic acid. For example, Horvath and co-workers reported a multistep process for the conversion of sucrose to LA and subsequent hydrogenation to GVL, 1, 4-pentandiol, 2-methyl−THF, and alkanes. LA/water solution with a yield higher than 95% was obtained with heterogeneous catalyst $Ru(acac)_3$/TPPTS at 140 °C and 10 MPa for 12 h.[11] Tang et al.[19] reported a green and efficient process of the conversion of ethyl levulinate into GVL. They used supercritical ethanol as the hydrogen donor and achieved a good GVL yield of 81.5% at 250 °C. Moreover, Elliott used a bifunctional PdRe/carbon catalyst to produce GVL at 200−250 °C and 10 MPa H_2.[20] Obviously, these routes are very attractive except for the drastic reaction conditions.[8] Although it is a well-established method for the synthesis of GVL, effective reduction of LA at mild conditions was proven to be very difficult.[21]

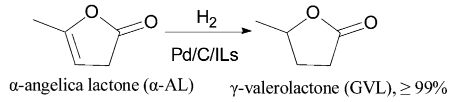
Received: December 9, 2013
Revised: January 13, 2014
Published: January 17, 2014

dx.doi.org/10.1021/sc4005185 | *ACS Sustainable Chem. Eng.* 2014, 2, 902−909

Meanwhile, α-angelica lactone (α-AL) was recently defined as a new platform molecule that can be produced from lignocellulosic material LA. And α-AL is widely used as a flavoring essence in the food and tobacco industry for its pleasant aromas. Also, the dehydration of LA to α-AL is easily accomplished by only setting the heating temperature to 160 °C,[20] while Hou et al. used SO_4^{2-}/ZrO_2 as a catalyst to convert LA at 100−150 °C and achieved a better yield of 95%.[22] Thus, it is clear to see that the synthetic method for α-AL is more and more easily achieved. However, there is rarely report available in the literature about the hydrogenation of α-AL.[20,23,24] Therefore, we consider using α-AL as the raw material to produce GVL with metal catalysts at mild reaction conditions. And this method for GVL formation provides a new option for the selective reduction of biomass derived molecules.

Recently, ionic liquids (ILs) as novel solvents with favorable environmental and technical features have attracted a lot of attention.[25,26] Extensive studies have been done on the applications of ILs as excellent green solvents in different types of reactions for their attractive physical and chemical properties,[25,27−29] especially in the conversion of biomass-derived carbohydrates.[30−32] For instance, Bogel-Łukasik et al.[32] summarized the achievements of different ILs in the synthesis of 5-HMF and pointed out that ILs broadened their application in biomass conversion as a promising alternative. Meanwhile, ILs have also been used as solvents in the selective hydrogenation of α, β unsaturated aldehydes by Anderson,[27] such as $[Bmim]PF_6$ and $[Bmim]BF_4$, they proved that the presence of ILs has again a promoting effect on the selective hydrogenation of the C═C bond compared with conventional molecular organic solvents. To the best of our knowledge, high conversion and selectivity are difficult to achieve in the synthesized process of GVL at mild conditions, and there is no report available in literature about hydrogenation of α-AL with ILs. Hence, we developed an effective method with Pd/C catalyst prepared by impregnation and ILs as solvents for the hydrogenation (Scheme 1) at room temperature. The reusability of ionic liquid/catalyst system is very good, which makes the atom economic route more practical and sustainable. The influence of corresponding factors and the kinetics as well as a possible mechanism on hydrogenation were investigated.

Scheme 1. Selective Hydrogenation of α-AL to GVL in Ionic Liquids



EXPERIMENTAL SECTION

Materials. α-Angelica lactone (97.0%) was purchased from Chifei Chemical Company, which was placed in a refrigerator to avoid isomerization to β-angelic lactone (β-AL). $PdCl_2$ was obtained from J&K Scientific Ltd. Hydrochloric acid (38 wt %) was purchased from Xilong Chemical. High purity (99.99%) H_2 was obtained from Beiwen Special Gas Factory, Beijing. Ionic liquids (Chengjie, Shanghai, 99.0%) were placed under vacuum at 60 °C to minimize water content before use.

γ-Valerolactone and α-angelica lactone were analytical purity and purchased from J&K Scientific Ltd. and used as the standards without any further purification. Acetonitrile of HPLC grade was provided by Fisher scientific, and pure water was obtained from Watsons, Beijing.

Catalyst Preparation. Palladium catalyst was prepared by impregnation on the carbon support with a 0.047 M solution of H_2PdCl_4. Activated carbon was coped with 30% HNO_3 before use. According to theoretical calculations, a certain amount of chloride precursors (H_2PdCl_4) was added into 3.0 g activated carbon dropwise which mixed with 60 mL distilled water at 60 °C. For deposition, aqueous Na_2CO_3 solution(2 mol/L) was added to the impregnating solution in order to maintain constant pH. After stirring for 8 h, the reduction was performed in liquid phase using formaldehyde at 80 °C for 2 h. Then, the catalyst was washed with 80 °C distilled water and dried in a vacuum oven for 18 h. Detailed information of the catalyst characterized by X-ray diffraction (XRD), Brunauer−Emmett−Teller (BET), scanning electron microscropy (SEM), transmission electron miscroscopy (TEM), and energy dispersive spectroscopy (EDS) can be found in the Supporting Information.

Hydrogenation Experiments and Analysis. All reactions were carried out in a 50 mL high-pressure reactor equipped with a safety relief and pressure gauge. In a typical experiment, 3 wt % catalyst (catalyst/α-AL weight ratio), 5.0 g ionic liquid, and 2.0 g (0.02 mol) α-AL were introduced to the autoclave in succession. Then, the autoclave was closed, and air was flushed out with nitrogen at room temperature. Hydrogen was then fed into the reactor to the desired pressure. The inlet value was then closed and heating commenced with stirring to avoid settling of the catalyst and the whole reaction maintained the stirring speed to ensure the absence of mass transfer limitations. When the reaction was complete, the autoclave was rapidly cooled, and the gas was discharged and the liquid mixture was immediately separated with catalyst by centrifuge. As for the recycling experiments for the ionic liquid-catalyst system, we used diethyl ether (6 × 10 mL) to extract product, and the lower phase was dried in a vacuum oven at 40 °C for 4 h. Then, the fresh reactant was added for the next experiment.

The products were analyzed by HPLC (Agilent 1100) fitted with a refractive index detector and an ODS-BP column (0.46 mm × 250 mm). The mobile phase was the mixture of acetonitrile and water with a ratio of 3:7; the mobile phase was sonicated for 30 min before use. The oven temperature for the determination of standards and samples was set at 40 °C with a flow rate of 0.8 mL/min.

RESULTS AND DISCUSSION

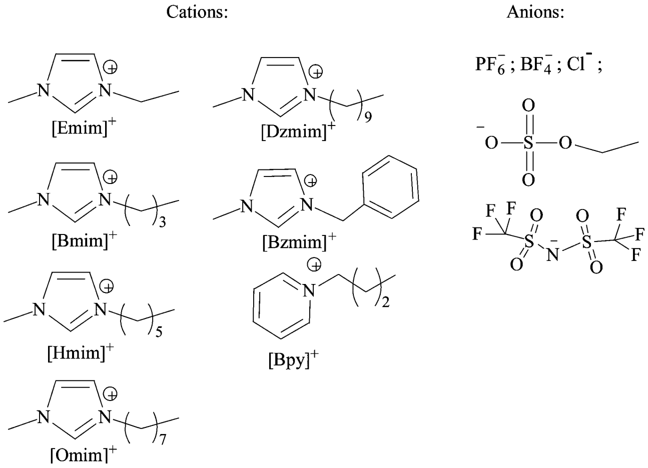
Selective Hydrogenation of α-AL. *Effect of Ionic Liquids.* Table 1 summarizes the results of α-AL hydrogenation in various ILs with different anions and cations (Scheme 2) at 4.0 MPa and 60 °C with Pd/C as the catalyst. As can be seen in the Table 1, the tests for ILs with same anions show that the conversion decreased with the increase of carbon chain of cations except [Emim] (Table 1, entry 1−5). The low conversion is due to the fact that $[Emim]PF_6$ is a solid at

Table 1. Effect of Ionic Liquids on the Selective Hydrogenation of α-AL[a]

	ionic liquids			
entry	cation	anion	α-AL conv (%)	GVL sel (%)
1	$[Emim]^+$	$[PF_6]^-$	44.6	80.9
2	$[Bmim]^+$	$[PF_6]^-$	57.5	99.8
3	$[Hmim]^+$	$[PF_6]^-$	46.9	70.9
4	$[Omim]^+$	$[PF_6]^-$	36.9	86.4
5	$[Dzmim]^+$	$[PF_6]^-$	17.7	99.1
6	$[Bmim]^+$	$[BF_4]^-$	41.9	95.8
7	$[Emim]^+$	$[EtOSO_3]^-$	84.9	32.4
8	$[Bzmim]^+$	$[HSO_4]^-$	1.9	99.9
9	$[Bzmim]^+$	Cl^-	26.1	58.5
10	$[Bpy]^+$	$[NTF_2]^-$	41.0	94.6

[a] Reaction conditions: T 60 °C, P_{H2} 4.0 MPa, t 20 min, α-AL 2.0 g (0.02 mol), ionic liquid 5.0 g, 10% Pd/C 0.06 g.

Scheme 2. Various Cations and Anions of Ionic Liquids



room temperature and difficult to form a homogeneous solution with the reactant. On the whole, the selectivity of GVL in $[PF_6]^-$ based ILs showed a better performance for all above 80%. Meanwhile, with the test of same cations, higher conversion and selectivity of $[Bmim]BF_4$ and $[Bmim]PF_6$ were observed (Table 1, entry 6), it can be concluded that $[Bmim]^+$ based ILs have a favorable effect on the hydrogenation of α-AL. The reaction with $[Emim]EtOSO_3$ showed the highest conversion of α-AL, but with a lower selectivity of 32.4% (Table 1, entry 7); this phenomenon was attributed to the excessive amount of hydrogen and a small amount of water, which easily led to the formation of valeric acid (VA) and LA.[16,33] Besides, poor results were obtained from acidic IL with the lowest conversion of 1.9% (Table 1, entry 8−10).

Therefore, considering the whole conversion and selectivity, the results obtained with $[Bmim]PF_6$ are obviously remarkable, which gave the highest conversion of 57.4% and selectivity of 99.8%. Moreover, Dupont[34] used $[Bmim]PF_6$ as a medium in the selective hydrogenation of olefins and also achieved a high conversion. It may be considered that $[Bmim]PF_6$ was a highly selective solvent for the C=C double bond hydrogenation.[27] It can be regarded that the solubility of H_2 in ILs highly affects the reaction, and the rate of mass transfer of hydrogen into ILs appears to be rapid.[35] Thus, further experiments have taken into account $[Bmim]PF_6$ as a solvent.

Effect of the Hydrogenation Catalysts. Many investigations have been demonstrated that metals, such as Pt, Ru, Cu, Au, Rh, Ni, and Pd, have positive effects on hydrogenation.[36−38] Therefore, carbon support 10 wt % Pd catalyst was prepared by impregnation method, and the comparison tests of various metal catalysts were performed in $[Bmim]PF_6$ at 60 °C with 20 min, and the obtained results of the hydrogenation of α-AL are shown in Figure 1. A 5.0% yield of GVL was obtained in the reaction without any catalyst. Besides, the yield of GVL was found to be 16.6% and 28.6% using Pt/C and non-noble metal Ni−Mo−Al as catalyst, while 10% Pd/C had a higher effect with the yield of 57.4%. Thereby, the results show that Pd/C is particularly active and selective for this reaction under the same conditions, comparing with the non-noble metal catalyst and Pt/C.

In the reaction, non-noble metal catalyst cannot be well dispersed into the solution because of agglomeration, which leads to lower surface area compared to carbon supported noble metal catalysts and, thus, results in the low conversion.

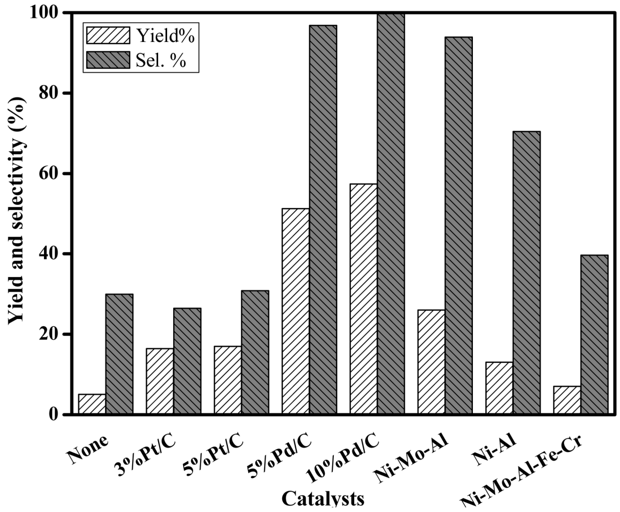


Figure 1. Effect of catalysts on the selective hydrogenation of α-AL in the presence of $[Bmim]PF_6$. Reaction conditions: T 60 °C, P_{H2} 4.0 MPa, t 20 min, α-AL 2.0 g (0.02 mol), $[Bmim]PF_6$ 5.0 g (0.0176 mol), catalyst 0.06 g.

Considering the low selectivity of GVL with Pt/C catalyst, it may be explained by the subsequent hydrogenation of GVL to VA.[16] The high surface areas and activity of 10% Pd/C is a key to increase the yield of GVL, and higher loading of Pd on activated carbon is another one to obtain high yield of GVL during the hydrogenation of α-AL. Thus, further studies on effects of reaction conditions on α-AL hydrogenation were carried out using 10% Pd/C catalyst and the results will be discussed below.

Effect of Temperature. The effects of temperature on α-AL hydrogenation were studied at constant pressure of 4.0 MPa, and the results are shown in Figure 2. From the obtained results, it can be concluded that the catalytic transformation of α-AL to GVL is sensitive to the temperature; while the temperature was raised from 25 to 100 °C, the yield of GVL increased from 30.2% and 96.4% with almost 100% selectivity. Kumelan[39] and Raeissi[40] found that hydrogen has a better dissolution in the ILs at higher temperature. Thus, it may be

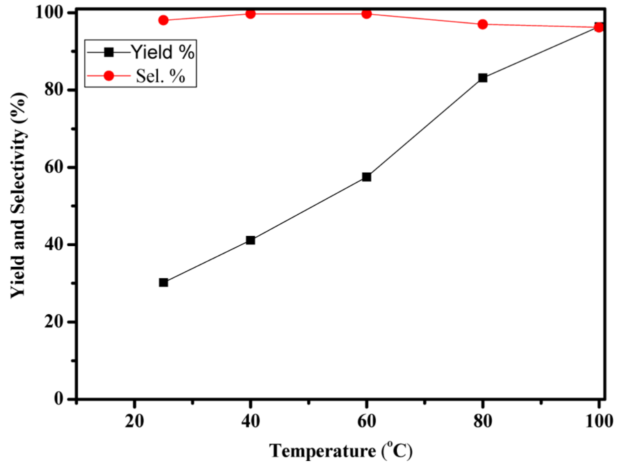


Figure 2. Effect of temperature on the hydrogenation of α-AL in the presence of Pd/C and $[Bmim]PF_6$. Reaction conditions: P_{H2} 4.0 MPa, t 20 min, α-AL 2.0 g (0.02 mol), $[Bmim]PF_6$ 5.0 g (0.0176 mol), 10% Pd/C 0.06 g.

concluded that higher temperature is helpful for the dissolution of hydrogen in [Bmim]PF_6.

Besides, there has a fact that the high temperature would promote a faster reaction rate and mass transfer of reactants as well as H_2. However, with the increase of temperature, the selectivity of GVL was slightly decreasing, and the produce of byproducts such as LA and VA increased. Therefore, the reaction temperature was set to 60 °C in further experiments.

Effect of Reaction Time. The effect of the reaction time on the yield of GVL is shown in Figure 3, which shows that the yield of GVL is obviously increased with reaction time. Only 57.4% of GVL was detected with a reaction time of 20 min, and over 60 min an amount of 88.5% was observed. In addition, the full conversion of α-AL to GVL was achieved after 100 min as shown in Figure 3. At constant temperature, the results demonstrate that the yield of GVL became higher for longer reaction time.

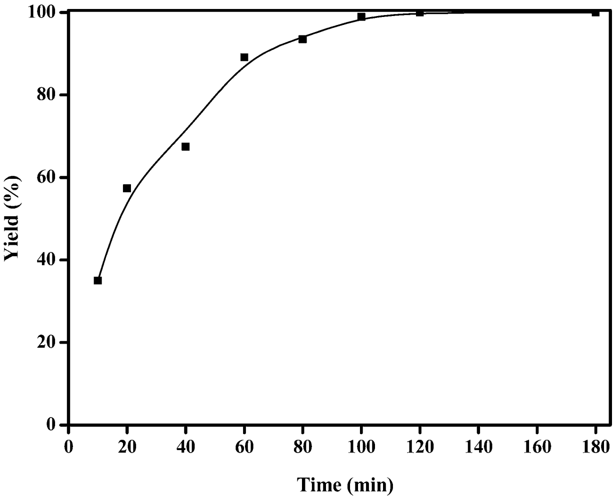


Figure 3. Effect of time on the hydrogenation of α-AL. Reaction conditions: *T* 60 °C, P_{H2} 4.0 MPa, α-AL 2.0 g (0.02 mol), [Bmim]PF_6 5.0 g (0.0176 mol), 10% Pd/C 0.06 g.

Effect of Hydrogen Pressure. Figure 4 presents the effect of hydrogen pressure on the yield in α-AL hydrogenation over 10% Pd/C. The pressure of H_2 strongly affects the reaction conversion, and GVL yield raised from 37.2% and 78.3% as the hydrogen pressure increased from 1.0 to 8.0 MPa. According to the previous literature,[39,40] the solubility pressure has a linear relationship with increasing molarity of hydrogen in the liquid phase. Thus, the rising yield with increase in hydrogen pressure was due to the higher dissolved concentration of hydrogen according to Henery's law.[36]

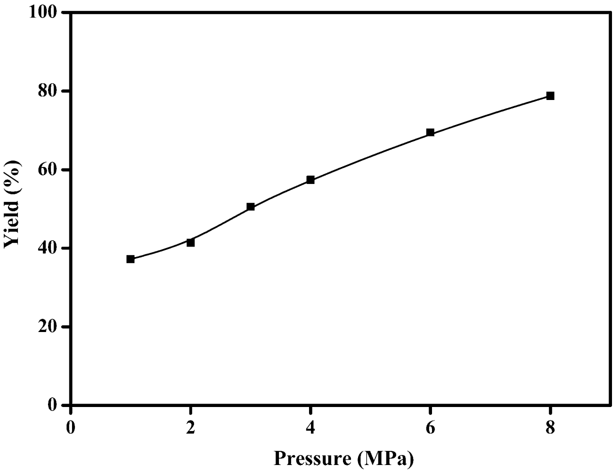


Figure 4. Effect of pressure on the hydrogenation of α-AL. Reaction conditions: *T* 60 °C, *t* 20 min, α-AL 2.0 g (0.02 mol), [Bmim]PF_6 5.0 g (0.0176 mol), 10% Pd/C 0.06 g.

Effect of Catalyst Loading. In order to select the appropriate amount of catalyst, the influence of different catalyst loading was investigated by varying the amount of the catalyst to α-AL ratio between 1.0 and 9.0 wt % at 60 °C and 4.0 MPa with 20 min, and the results are shown in Figure 5. It was found that the yield of GVL increased from 41.2% and 74.1% with the increase in catalyst loadings. Significantly, the obtained results show little change of GVL's yield after catalyst loading of 7%; that is to say, the surface adsorption of catalyst has achieved saturation. The increase in yield with increase in catalyst loading may be due to more availability of the active sites on the catalyst surface for the reaction. From the viewpoint of economy, the amount of 3 wt % was selected as an appropriate catalyst loading.

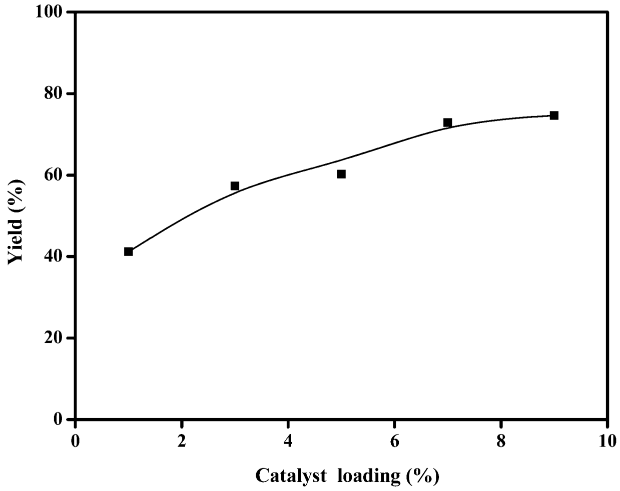


Figure 5. Effect of catalyst loading on the hydrogenation of α-AL. Reaction conditions: *T* 60 °C, P_{H2} 4.0 MPa, *t* 20 min, α-AL 2.0 g (0.02 mol), [Bmim]PF_6 5.0 g (0.0176 mol).

Selective Hydrogenation of α-AL to GVL in [Bmim]PF_6 at Room Temperature. From the above discussion, it was concluded that high temperature and pressure were helpful for the conversion of α-AL.

Therefore, in order to reduce energy consumption and handle the process easily in practice, the hydrogenation reaction was conducted under room temperature with 4.0 MPa H_2. The results show that GVL has a considerable yield with 99.9% at room temperature with a longer reaction time of 180 min in Figure 6. So it can be concluded from the above that the presence of [Bmim]PF_6 has a significant influence on the reaction of the selective hydrogenation at room temperature.

Recycle of the Ionic Liquid–Catalyst System. The feasibility of the IL and catalyst recycling was determined under conditions of 25 °C and 180 min. Once the first reaction completed, the mixture was extracted 6 times with 10 mL diethyl ether, and the upper phase was carefully removed; then, a fresh aqueous layer containing α-AL was added into the lower phase. As it is clear from the result of Figure 7, the system is

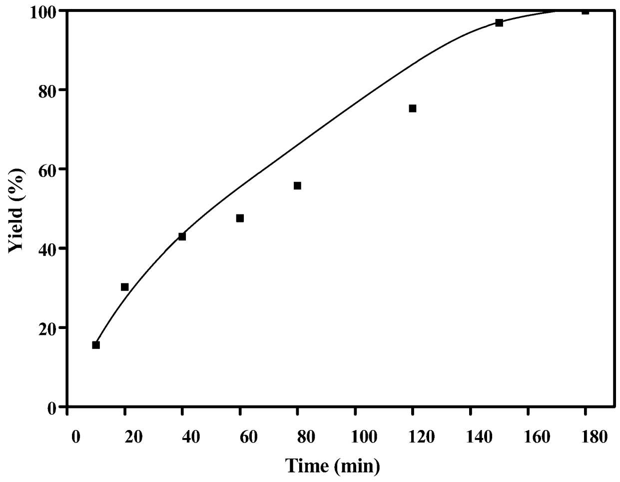


Figure 6. Effect of time on the hydrogenation of α-AL at room temperature. Reaction conditions: T 25 °C, P_{H2} 4.0 MPa, α-AL 2.0 g (0.02 mol), [Bmim]PF_6 5.0 g (0.0176 mol), 10% Pd/C 0.06 g.

equally active in the tenth run as in the first run with no decrease in conversion and selectivity on recycling.

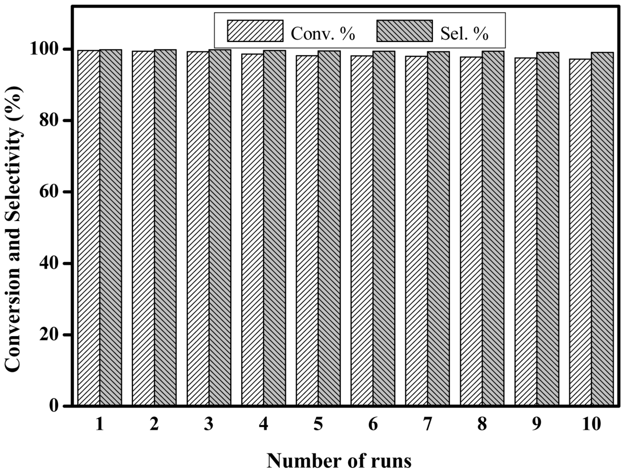


Figure 7. Recycling study of α-AL hydrogenation. Reaction conditions: T 25 °C, P_{H2} 4.0 MPa, α-AL 2.0 g (0.02 mol), [Bmim]PF_6 5.0 g (0.0176 mol), Pd/C 0.06 g.

Therefore, this trend proves one of the major advantages that ILs as solvents can be reused with minimal waste compared with organic solvents. Pd/C catalyst stayed in the IL stably, and no detectable leaching of the catalyst took place. Meanwhile, the particle size and size distribution of the recovered catalyst showed no obvious change and no agglomeration according to the SEM characterization (Supporting Information Figure S3).

Kinetics of Hydrogenation of α-AL. Various kinetic studies on the catalytic hydrogenation using a range of biomass materials have been reported in the literature.[41] For example, Weingarten et al.[42] studied the kinetic of LA to GVL from glucose using aqueous-phase acid catalyst in a batch reactor. They developed a kinetic model with a good fit to the experimental data in a batch reactor, which was also applicable for a plug flow reactor and continuously stirred tank reactor. Wu[43] studied the solubility of the hydrogen in LA and discovered that the overall hydrogenation reaction rate was first-order in hydrogen. But the studies of the kinetics of the hydrogenation of α-AL to GVL are extremely scarce and no kinetic modeling work about α-AL hydrogenation has been published so far. Besides, the kinetics data can provide a direct comparison with other catalysts and experimental conditions of α-AL hydrogenation and is also very important for the optimization reactor. Therefore, developing an appropriate kinetic model is absolutely essential for the kinetics of the hydrogenation of α-AL to GVL.

The heterogeneous catalysis always occurs on the surface of the catalyst.[44] Thus, in order to consider the effect of substrate concentration on the reaction kinetic, the reactor was filled with excessive hydrogen through all kinetic experiments to avoid the influence of hydrogen pressure. And we kept the experiments being carried out in a batch-type reactor at 20−100 °C in [Bmim]PF_6 with Pd/C at constant pressure. Therefore, the conversion rate of α-AL can be given by eq 1:

$$r = -\frac{\mathrm{d}c}{\mathrm{d}t} = k_1 C_{\alpha\text{-AL}}{}^{a} P_{H_2}{}^{b} \tag{1}$$

When the pressure was kept constantly at 4.0 MPa, $P_{H_2}{}^{b}$ of the equation can be considered as a constant. Consequently, the equation may be simplified as follows:

$$r = -\frac{\mathrm{d}c}{\mathrm{d}t} = k C_{\alpha\text{-AL}}{}^{a} \tag{2}$$

Meanwhile, the relationship of the concentration of α-AL with different time is shown in Figure 8. The obvious results show that $\ln(C_{\alpha\text{-AL}})$ has a linear relationship with time; thus, the reaction rate constants of different temperature from 20 to 100 °C can be seen from Table 2 and Figure 9. Therefore, our model assumed a first-order dependence with respect to the α-

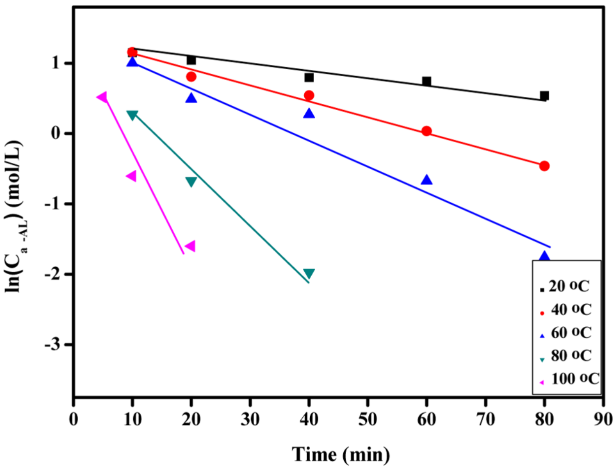


Figure 8. α-AL concentration vs time profiles at different temperatures. Reaction conditions: P_{H2} 4.0 MPa, α-AL 2.0 g (0.02 mol), [Bmim]PF_6 5.0 g (0.0176 mol), Pd/C 0.06 g.

Table 2. Reaction Rate Constants (k) at Various Temperatures for the Conversion of α-AL to GVL

T/°C	T/K	k	$T^{-1}/(10^{-3} \cdot K^{-1})$	$\ln(k)$
20	293.15	0.0104	3.4112	−4.5621
40	313.15	0.0222	3.1934	−3.8099
60	333.15	0.0373	3.0017	−3.2890
80	353.15	0.0736	2.8317	−2.6088
100	373.15	0.1231	2.6799	−2.0949

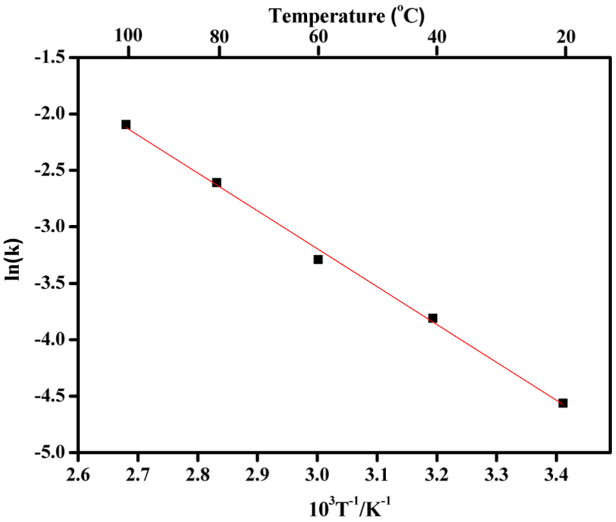


Figure 9. Temperature dependence of rate constants. Reaction conditions: P_{H2} 4.0 MPa, α-AL 2.0 g (0.02 mol), [Bmim]PF_6 5.0 g (0.0176 mol), Pd/C 0.06 g.

AL concentration. The activation energy (E_a) and pre-exponential factor (A) can be obtained from the slope and intercept,[45] respectively. Then, the estimated kinetic parameters for α-AL conversion appear in Table 3 according to the Arrhenius equation:

$$k = Ae^{-E_a/RT} \tag{3}$$

Here, A is the pre-exponential factor, R is the ideal gas constant, and E_a is the activation energy.

Table 3. Estimated Kinetic Parameters for the Conversion of α-AL to GVL

rate constant	A (min^{-1})	E_a (kJ/mol)
k	968.6	27.9

According to the estimated kinetic parameters, the kinetic equation can be expressed by eq 4:

$$-\frac{dc}{dt} = A\exp^{(-E_a/RT)}\, C_{\alpha\text{-AL}}{}^{a} = 968.6\exp\left(-\frac{27900}{RT}\right)C_{\alpha\text{-AL}} \tag{4}$$

Mechanism for α-AL Hydrogenation. The mechanism of α-AL hydrogenation itself was not clear, and there were no literature works about the mechanism of α-AL hydrogenation. Herein, one plausible explanation was proposed (Scheme 3). α-AL is very unstable and easily isomerizes to β-AL, and this isomerization process is very rapid at high temperature.[22] The hydrogenation of AL to form GVL is rationalized in terms of the following steps: (1) isomerization of α-AL; (2) absorption of C=C bond on the surface of Pd leading to the formation of a π-complex, which in turn can activate a dihydrogen molecule coordinated to the same palladium atom;[46,47] (3) absorption of H_2 on the surface of Pd and dissociation into highly active H-atom;[47] (4) attack of the activated C=C bond of the pentaheterocycles by the weakly held molecular hydrogen, from which the reductive elimination produces a GVL molecule and leads to the regeneration of the active site thereafter.[48] Due to the presence of carbonyl group, Pd of γ-position is removed first, then the β-position.[49,50]

CONCLUSIONS

We described an efficient process for the hydrogenation of α-AL to GVL by using Pd/C as the catalyst prepared by impregnation, and [Bmim]PF_6 as the solvent under very mild reaction conditions. The study shows that [Bmim]PF_6 can be served as a highly selective solvent for the C=C double bond hydrogenation compared with other ionic liquids. In addition, according to the effect of various factors, it is easy to achieve a complete conversion and nearly 100% selectivity of α-AL at room temperature. Meanwhile, the reaction system showed good reusability; after 10 uses there was no obvious decrease in conversion and selectivity. The kinetic study was performed under optimized conditions, and the results have proven that the catalytic hydrogenation of α-AL is a first-order reaction in [Bmim]PF_6 under constant pressure. The kinetic parameters (E_a, A) and kinetic equation were obtained, and the value of two parameters were 27.9 kJ/mol and 968.6 min^{-1}, respectively. The kinetic model was also proved to be reliable through the experiments.

ASSOCIATED CONTENT

Supporting Information

Characterization data of catalyst: BET, XRD, TEM, SEM, and EDS. This material is available free of charge via the Internet at http://pubs.acs.org.

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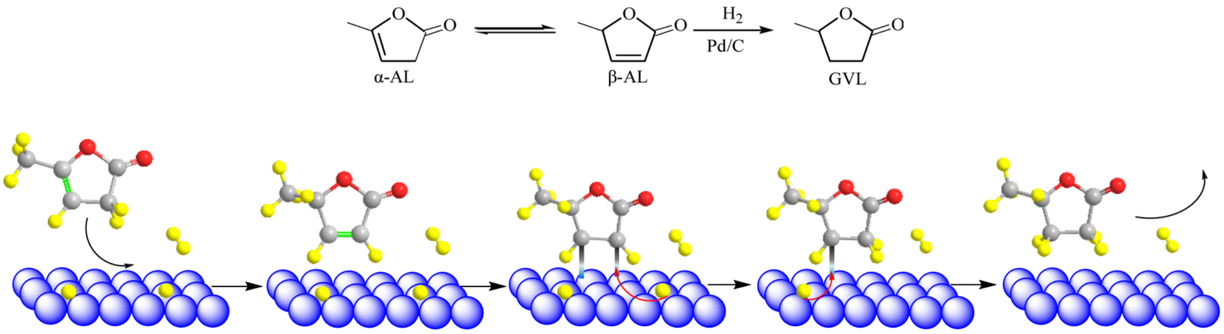
Notes

The authors declare no competing financial interest.

Scheme 3. Predictive Mechanism for α-AL Hydrogenation



ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China (Nos. 21210006, 21336002, 21006112, and 21276260) and the Key Project of the Natural Science Foundation of Beijing of China (No. 2131005). We thank Prof. Z. Conrad Zhang for helpful discussion.

ABBREVIATIONS

α-AL, α-angelica lactone
β-AL, β-angelica lactone
ILs, ionic liquids
LA, levulinic acid
GVL, γ-valerolactone
VA, valeric acid

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