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Biomass Conversion

Production of γ-Valerolactone from One-Pot Transformation of Biomass-Derived Carbohydrates Over Chitosan-Supported Ruthenium Catalyst Combined with Zeolite ZSM-5

Tianlong Wang,[a] Jianghua He,*[a] and Yuetao Zhang*[a]

Abstract: It remains as a challenge to directly transform the biomass-derived C5 carbohydrates, such as furfural (FF) and its upstream product xylose and hemicellulose, to γ-valerolactone (GVL), a versatile renewable chemical platform, due to various restrictions in the current synthetic strategies. Using formic acid as green hydrogen source, we synthesized the recyclable chitosan-Ru/PPh_3 catalyst system, effective for both the hydrogenation of FF to furfuryl alcohol (FAL) and the reduction of levulinic acid (LA) or ethyl levulinate (EL) to GVL, affording up to 99 % product yields. The combination of chitosan-Ru/PPh_3 with ZSM-5 could successfully achieve up to 79 % yield of GVL from one-pot conversion of FF under mild condition. Preliminary studies indicated that this method could also be applied to the direct conversion of biomass-derived C5 carbohydrates such as xylose and hemicellulose to GVL in 37 % or 30 % yield, respectively.

Introduction

As one of three important components (cellulose, hemicellulose and lignin) in lignocellulosic biomass,[1] hemicellulose is highly underutilized.[2] Furfural (FF), the main products obtained from hemicellulose, is considered as one of the top ten value-added platform chemicals[3] for production of energy fuels and various useful chemicals such as furfuryl alcohol (FAL),[4] furoic acid,[5] 2-methylfuran,[6] maleic anhydride,[7] γ-valerolactone (GVL)[8] etc. Among these, GVL is of particular interests since it could serve as a versatile biomass-derived platform chemical due to its excellent properties as green solvent[9] and fuel additive as well as precursor for the synthesis of various liquid alkenes[10] and renewable biopolymers.[11] Compared with fructose derived from cellulose, FF originated from hemicellulose is more suitable for the production of GVL and exhibits better carbon atom economy since it does not lose one carbon during the production of levulinic acid (LA).[12] In general, several steps are required for the production of GVL including the hydrogenation of FF to FAL,[13] the subsequent alcoholysis of FAL to LA or alkyl levulinate,[14] and then hydrogenation of LA or alkyl levulinate to corresponding 4-hydroxypentanoates (4-HPs), followed by the lactonization of 4-HPs to generate GVL.[15] For economic and cost-saving purpose, it is more desirable to produce GVL from one-pot conversion of the abundant biomass-derived C5 carbohydrates such as furfural, xylose and hemicellulose. However, only a handful of catalyst systems have been developed to accomplish this goal so far.[16–20] Such as Román-Leshkov and co-workers achieved a 78 % yield of GVL from the domino reaction catalyzed by zeolites with both Brønsted and Lewis acid catalyst sites in 2013.[16] Later, bifunctional Zr-Al-Beta zeolite prepared through a post-synthetic route obtained GVL in 22.6 % or 34 % yield from one-pot conversion of FF or xylose in 2-propanol, respectively.[17] The combination of Au/ZrO_2 and ZSM-5 could achieve an 80.4 % yield of GVL from one-pot conversion of FF.[18] In 2018, hafnium-based metal-organic frameworks was combined with Brønsted-acidic Al-beta zeolite to furnish a 75 % yield of GVL from one-pot conversion of FF.[19] Heteropoly acid supported on Zr-Beta zeolite was also reported to obtain GVL in 68 % yield from one-pot transformation of FF.[20]

To avoid using high-pressure H_2 (> 30 bar) as hydrogen source like cellulose protocol did,[12a] it is essential to explore green hydrogen sources for the production of biomass-derived GVL. In addition to 2-propanol employed in the Meerwein–Ponndorf–Verley reduction, formic acid (FA) is also considered to be an alternative and renewable hydrogen source for hydrogenation reaction, such as the reduction of unsaturated C=C[21] and C=O bond,[22] exhibiting better performance than gaseous hydrogen due to its high hydrogen density and easy access from the hydrogenolysis of cellulose.[23] Both the homogeneous and heterogeneous ruthenium(Ru)-based catalyst could promote the decomposition of HCOOH for the production of GVL from LA. Such as a recyclable $RuCl_3$/PPh_3/pyridine catalyst system produced an 95 % yield of GVL from LA[22d] whereas Ru/C catalyst furnished a 57 % yield of GVL from LA.[24] However, no bio-derived, recyclable Ru-based catalyst was reported

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[a] *State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University,*
Changchun, Jilin 130012, China
E-mail: hjh2015@jlu.edu.cn
ytzhang2009@jlu.edu.cn
Yuetao Zhang: http://supramol.jlu.edu.cn/info/1030/1894.htm
Jianghua He: http://chem.jlu.edu.cn/info/1029/3915.htm?admin=admin

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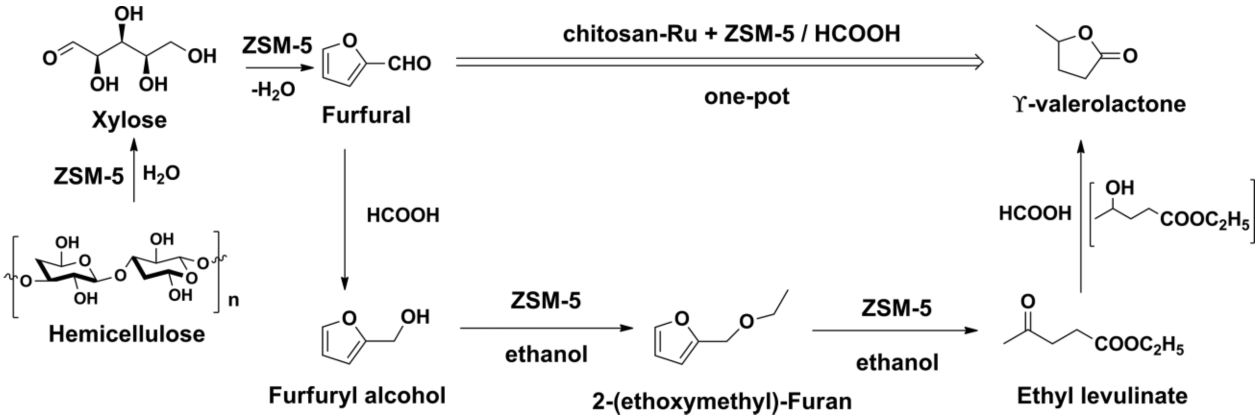


Scheme 1. One-pot conversion of FF (xylose, hemicellulose) to GVL by chitosan-Ru/PPh_3 combined with ZSM-5.

for conversion of the biomass-derived C5 carbohydrates to GVL by using HCOOH as green hydrogen source so far.

As a biodegradable and inexpensive amino-polysaccharide with high binding affinity for transition-metal ions,[25] chitosan is commonly employed as catalyst support to generate heterogeneous chitosan supported metal complexes (chitosan-M) for various catalytic applications in organic synthesis.[26] We envisioned that the employment of biomass-derived chitosan-M might enable us to achieve one-pot conversion of FF to GVL by using HCOOH as hydrogen source. Here we synthesized a series of chitosan-M (M = Ru, Pd, Co, Ni) and found that chitosan-Ru/PPh_3 system is highly effective for both the hydrogenation of FF to FAL and reduction of LA/alkyl levulinate to GVL, achieving up to 99 % product yield by using HCOOH as hydrogen source. The combination of chitosan-Ru/PPh_3 with ZSM-5 zeolite (Scheme 1) successfully achieved one-pot transformation of biomass-derived carbohydrates such as FF as well as its upstream product such as xylose or hemicellulose to GVL in 79 %, 37 %, or 30 % yield, respectively. Corresponding reuse and recycle experiments were also included in this study.

Results and Discussion

Catalyst Characterization

After the synthesis of chitosan-Ru (check experimental section for details), we collected filtrate and recrystallized it with acetone to furnish white solids in 88 % yield. Upon heating the obtained white solids in NaOH solution, the wet red litmus paper became blue color revealed the existence of ammonium ions in the filtrate. Adding white solids to $AgNO_3$ solution acidified by HNO_3 led to the formation of white flocculent precipitates immediately, which suggested that the chloride ions of $RuCl_3$ was retained in the filtrate rather than on the synthesized chitosan-Ru and the obtained white solids should be NH_4Cl. It should be noted that NH_4Cl was generated from the neutralization of HCl released from the reaction of chitosan with $RuCl_3$ by ammonia ($NH_3{\cdot}H_2O$). FT-IR spectra of the synthesized chitosan-Ru complex and chitosan (Figure 1a) indicated that chitosan-Ru maintained the similar framework with that of chitosan. The peak centered at 3433 cm^{-1} attributed to the stretching vibration of amino and hydroxyl group in chitosan was shifted to the broader peak centered at 3371 cm^{-1}, and the 1420 cm^{-1} peak in the chitosan[25] belong to the bending vibration of –OH also weakened, which suggested the coordination of Ru ions to the N and O atom in the chitosan-Ru. As shown in XPS characterization of the chitosan-Ru (Figure 1b), energy peaks at 463.9 and 486.1 eV were attributed to the Ru^{3+} $3p_{1/2}$ and $3p_{3/2}$ bands, which further revealed that Ru species is trivalent.[27] As shown in Figure 1c, powder XRD spectra of chitosan-M and the recovered chitosan-Ru catalyst revealed that the fresh-prepared is similar with that of the recovered chitosan-Ru. According to ICP measurement (Table S1), the corresponding metal loading in chitosan-M (M = Ru, Pd, Co, Ni) is 6.14 wt.-% for Ru, 5.18 wt.-% for Pd, 5.82 wt.-% for Co and 5.40 wt.-% for Ni, respectively. TG analysis (Figure 1d) revealed that the framework of both the synthesized chitosan-Ru complex and chitosan could be maintained up to 200 °C**.** The CO_2 and NH_3-temperatured program desorption (TPD) spectra showed that the biomass-derived chitosan-Ru had both acidic and basic catalyst sites (Figure S5), which are significantly important for the decomposition of FA and the subsequent hydrogenation reaction.[28]

Catalytic Hydrogenation of the C=O Bonds in FF and Other Substrates

Using FF as substrate and HCOOH as hydrogen source, control experiments showed that chitosan is completely ineffective for hydrogenation of FF to FAL (entry 1, Table 1) while chitosan-Ru only obtained 33 % yield of FAL at 120 °C for the hydrogenation of FF (entry 2, Table 1), which implied that both chitosan and chitosan-Ru are not efficient catalysts for the decomposition of FA. Therefore, a series of additives were examined for their effectiveness on the reaction (Table S2). It turned out that the highest FAL yield of 99 % was achieved by the combination of triphenylphosphine (PPh_3) with chitosan-Ru (entry 1, Table S2). It is also noted that solvents with medium polarity (i.e. CH_2Cl_2, ethanol, THF) exhibited comparable activity towards the decomposition of formic acid and the subsequent hydrogenation reaction. However, solvents with the higher or lower polarity such as DMF and TOL would drastically slow down the reaction

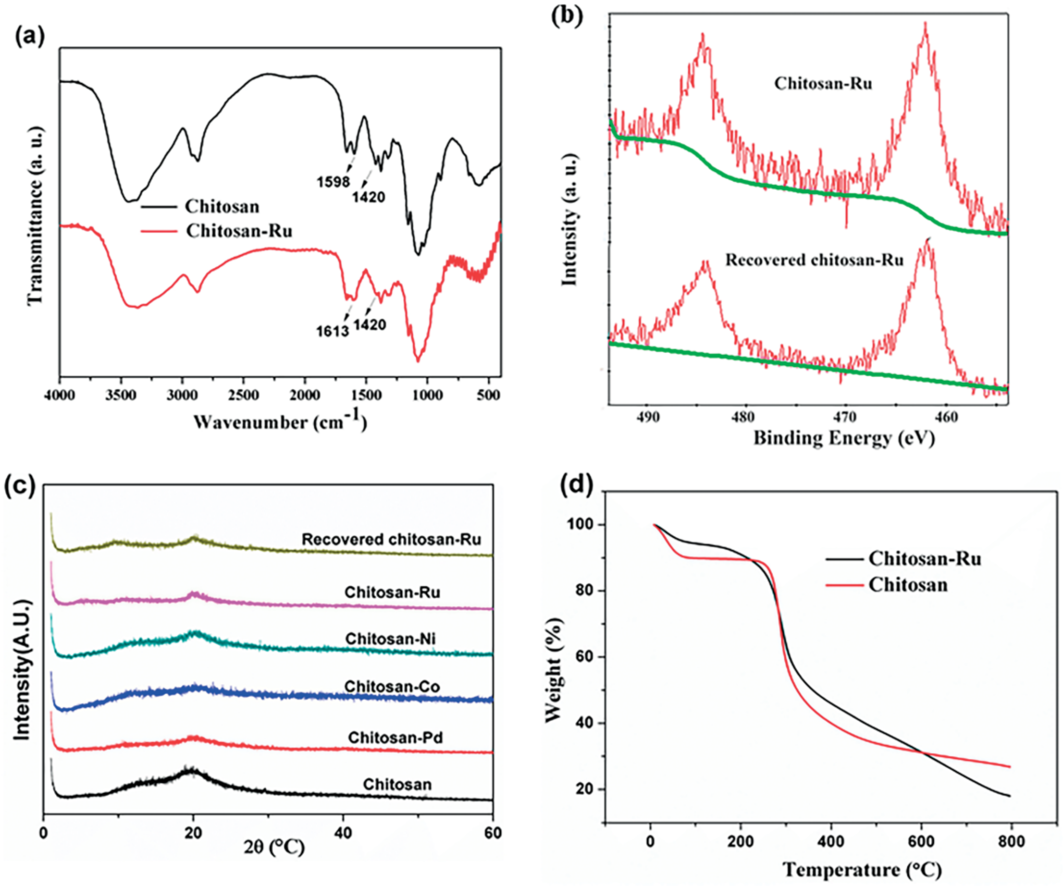
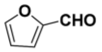
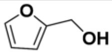
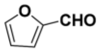
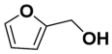
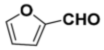
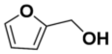
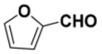
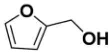
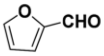
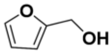
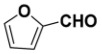
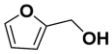
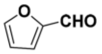
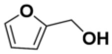
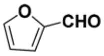
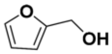
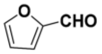
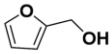
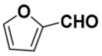
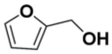
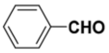
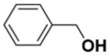
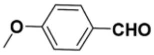
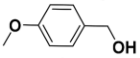
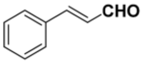
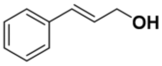
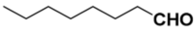
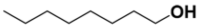
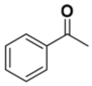
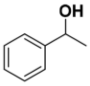
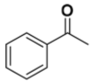
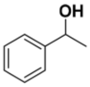
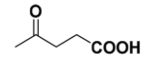
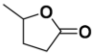
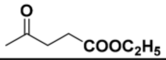
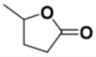


Figure 1. (a) FT-IR spectra of chitosan-Ru and chitosan; (b) XPS spectra of chitosan-Ru and recovered chitosan-Ru from the transformation of FF to FAL; (c) overlay of Powder XRD spectra of chitosan and various chitosan-M complexes; (d) TGA curves of chitosan and chitosan-Ru.

(Table S3). THF displayed the best catalytic performance among the investigated solvents. Combined with the screening results of the other parameters (Tables S2 and S3), hydrogenation of FF was carried out with a 3 mol-% catalyst loading, 8 mg of PPh_3 and 5 equiv. HCOOH at 120 °C to examine the effectiveness of different catalysts in THF. In sharp contrast to chitosan-Ru, neither chitosan-Co nor chitosan-Ni works for the reaction (entries 4 and 5, Table 1) and chitosan-Pd only obtained 10 % FAL yield (entry 6, Table 1). The reactivity difference between these chitosan-M (M = Co, Ni, Pd) and chitosan-Ru might be attributed to their metallicity differences resulting from the different metal centers.[21a,29] The employment of $RuCl_3$ obtained 30 % yield of FAL (entry 8, Table 1), which may due to the absence of base additive. Previous studies indicated the employment of Ru^0/C as catalyst achieve 80.7 % GVL yield from LA in the presence of FA, but with the requirement of Et_3N.[30] In sharp contrast, only 8 % yield of FAL was obtained by zero-valent ruthenium support on carbon (Ru/C, entry 7, Table 1), which might be attributed to the absence of basic sites in Ru/C. It is noted that the hydrogen source is also essentially important to the hydrogenation of FF. Replacing HCOOH with HCOONa only furnished 6 % yield of FAL (entry 10, Table 1) while using 10 bar H_2 as hydrogen source will quench the hydrogenation reaction (entry 9, Table 1), which indicated that the hydrogenation of FF was through hydrogen transfer rather than by the H_2 decomposed from FA. With the identification of the excellent hydrogenation system of chitosan-Ru/PPh_3, we further expanded the scope of substrates for hydrogenation and achieved above 95 % alcohol yields for all substrates with a C=O bond (entries 11-16, Table 1). The fact that a 95 % yield of cinnamyl alcohol was obtained for the hydrogenation of cinnamaldehyde indicated the excellent selectivity of chitosan-Ru/PPh_3 catalyst system for the reduction of aldehyde groups (C=O) rather than C=C under such condition (entry 13, Table 1). Moreover, chitosan-Ru/PPh_3 only obtained in 10 % yield from the hydrogenation of acetophenone after heated at 120 °C for 8 h (entry 15, Table 1). Increasing reaction temperature to 160 °C resulted in the significantly enhanced yield of 98% for 1-phenylethanol (entry 16, Table 1). These results prompted us to apply the chitosan-Ru/PPh_3 catalyst system to the hydrogenation of levulinic acid (LA) and ethyl levulinate (EL). Similar to the reduction of acetophenone, hydrogenation of LA with HCOOH performed at 120 °C only afforded GVL in 20 % yield (entry 1, Table S4), probably due to the absence of conjugated system and larger steric hindrance of ketone structure in LA than that of aldehyde group in FF.[31] Increasing reaction temperature resulted in the significantly enhanced GVL yield (140 °C, 56 %, entry 2, Table S4 and 160 °C, 99 %, entry 17, Table 1). Switching to EL, a 97 % GVL yield were achieved under similar condition (entry 18, Table 1). These results further

Table 1. Transfer hydrogenation using FA as hydrogen source.[a]

Entry	Substrate	Product	Catalyst	Additive	Temp (°C)	Time (h)	Yield[b] (%)
1			Chitosan	no	120	1.5	0
2			Chitosan-Ru	no	120	1.5	33
3			Chitosan-Ru	PPh_3	120	1.5	99
4			Chitosan-Co	PPh_3	120	1.5	0
5			Chitosan-Ni	PPh_3	120	1.5	0
6			Chitosan-Pd	PPh_3	120	1.5	10
7			Ru/C	PPh_3	120	1.5	8
8			$RuCl_3$	PPh_3	120	1.5	30
9			Chitosan-Ru	PPh_3	120	1.5	3[c]
10			Chitosan-Ru	PPh_3	120	1.5	6[d]
11			Chitosan-Ru	PPh_3	120	1.5	98
12			Chitosan-Ru	PPh_3	120	1.5	98
13			Chitosan-Ru	PPh_3	120	1.5	95
14			Chitosan-Ru	PPh_3	120	1.5	99
15			Chitosan-Ru	PPh_3	120	8	10
16			Chitosan-Ru	PPh_3	160	8	98
17			Chitosan-Ru	PPh_3	160	8	99
18			Chitosan-Ru	PPh_3	160	8	99

[a] Conditions: 0.5 mmol substrate, 3 mol-% catalyst, 6 mol-% PPh_3, 5 equiv. FA in 1 mL THF. [b] Yield was determined by GC analysis using naphthalene as internal standard. [c] H_2 as hydrogen source instead of HCOOH. [d] HCOONa was used as hydrogen source instead of HCOOH.

demonstrated the excellent catalytic performance of chitosan-Ru/PPh_3 system on the hydrogenation of LA or EL to GVL.

Production of GVL from One-Pot Conversion of FF, Xylose and Hemicellulose to GVL

The successes achieved in the hydrogenation of FF and reduction of LA or EL inspired us to examine the effectiveness of chitosan-Ru/PPh_3 system for one-pot conversion FF to GVL in THF. However, no GVL was produced probably due to the absence of effective reagent for the alcoholysis of FAL to alkyl levulinate (AL) during the conversion of FF to GVL. The use of ethanol as solvent still did not obtain GVL, producing FAL in 96 % yield instead (entry 1, Table 2). According to the reaction route (Scheme 1), Brønsted acidic catalyst is required to promote the alcoholysis of FAL to AL in the tandem conversion of FF to GVL. Since chitosan-Ru/PPh_3 system is highly effective for both the hydrogenation of FF to FAL and reduction of LA (or AL) to GVL (achieving up to 99 % product yield for both case), we envisioned that an effective, Brønsted acidic alcoholysis reagent might be the missing piece from the chitosan-Ru/PPh_3 catalytic system to enable us to accomplish one-pot conversion of FF to GVL. After digging literature, we found that commercially available, acidic zeolite ZSM-5 is highly effective for the transformation of FAL to AL[32] and the mechanism of alcoholysis of FAL to allyl levulinate by Brønsted acid catalyst has also been studied.[33] Therefore, acidic zeolite ZSM-5 was employed to combine with chitosan-Ru/PPh_3 system and ethanol was used as both green solvent and alcoholysis reactant for the tandem conversion of FF to GVL. We systematically investigated the influences of the dosage of FA, ZSM-5, chitosan-Ru catalyst, and PPh_3 on one-pot conversion of FF heated at 160 °C for 30 h (Figure 2). It turned out the optimal results were achieved by the experiment performed with 3 mol-% catalyst loading of chi-

Table 2. One-pot conversion of FF, xylose and hemicellulose to GVL.[a]

Entry	Substrate	Catalyst	Other product, yield[b] [%]	GVL yield[b] [%]
1	FF	Chitosan-Ru	FAL, 96	0
2	FF	Chitosan-Ru/ZSM-5(Si:Al = 25)	EL, < 1	79
3	FF	Chitosan-Ru/ZSM-5(Si:Al = 80)	EL, 24	44
4	FF	Chitosan-Ru/ZSM-5(Si:Al =200)	EL, 32	34
5[c]	xylose	Chitosan-Ru/ZSM-5(Si:Al = 25)	EL, < 1	26
6[d]	xylose	Chitosan-Ru/ZSM-5(Si:Al = 25)	EL, < 1	37
7[c]	hemicellulose	Chitosan-Ru/ZSM-5(Si:Al = 25)	EL, < 1	23
8[d]	hemicellulose	Chitosan-Ru/ZSM-5(Si:Al = 25)	EL, < 1	30

[a] Conditions: 0.5 mmol FF, 3 mol-% catalyst, 8 mg of PPh_3, 200 mg of ZSM-5 (except entry 1) and 5 equiv. FA in 1.2 mL ethanol, heated at 160 °C for 30 h. [b] Yield were determined by GC analysis using naphthalene as internal standard. [c] Heated at 170 °C for 30 h. [d] Addition of 10 equiv. of H_2O and heated at 170 °C for 30 h.

tosan-Ru, 8 mg of PPh_3, 200 mg of ZSM-5 (Si:Al = 25:1) and 5 equiv. FA, furnishing 79 % GVL yield (Entry 1, Table 2). It should be noted that in the presence of PPh_3, chitosan-Ru could achieve 99 % product yield from the hydrogenation of FF to FAL at 120 °C and transformation of LA or AL to GVL at 160 °C whereas only 80 % yield of GVL was obtained for one pot conversion of FF at 160 °C, which might be attributed to the formation of humins, resulting from the self-polymerization of furfural at high temperature.[34] Previous studies indicated that PPh_3 can act as an electron-donor additive[35] and have a weak interaction with Ru^{3+} ions, which can facilitate the decomposition of FA, thus being beneficial for the hydrogenation.[36] Therefore, the presence of PPh_3 is also crucially important for the reaction. Without PPh_3, only 30 % yield of GVL could be produced from one-pot conversion of FF. As far as ZSM-5 is concerned, its strong Brønsted acidity enabled us to successfully achieve one-pot conversion of FF to GVL by connecting the hydrogenation of FF to FAL and transformation of AL to GVL. Furthermore, the employment of ZSM-5 (Si:Al = 25, entry 2, Table 2) with the lower Si/Al ratio exhibited better catalytic performance than that by ZSM-5 with higher Si/Al ratio (Si:Al = 80 or 200, entries 3 and 4, Table 2), indicating the higher content of Al atom

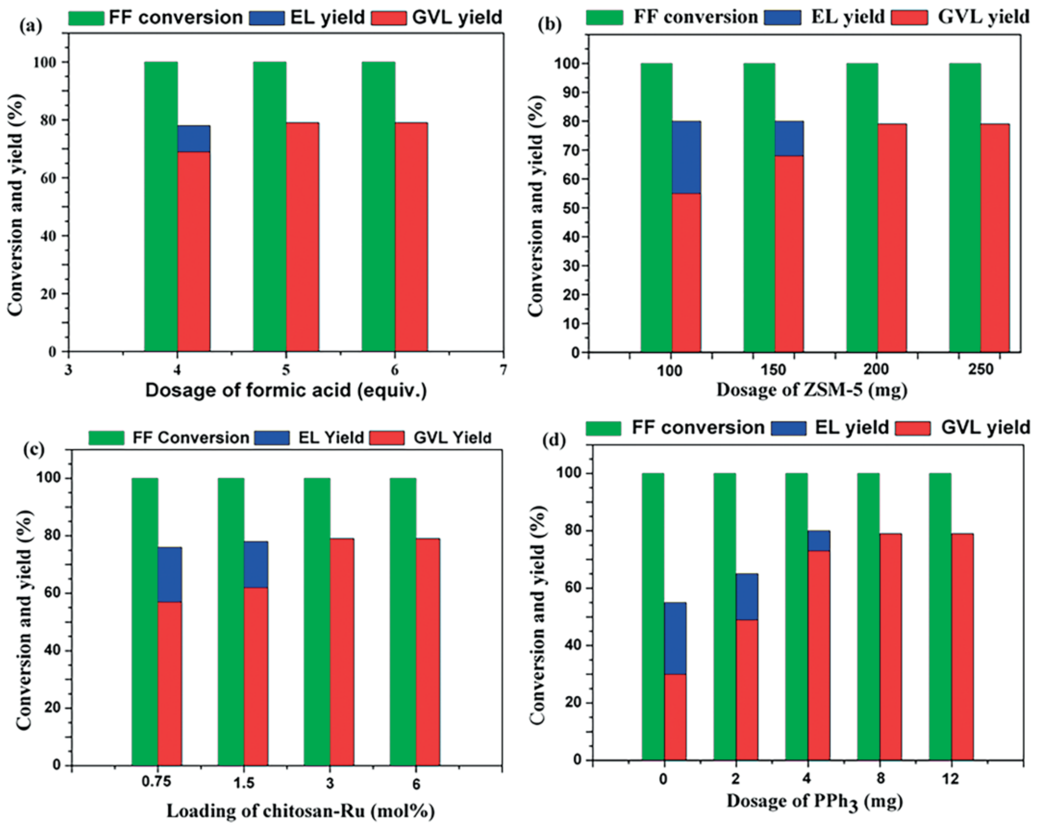


Figure 2. Effect of the dosage of FA, ZSM-5, chitosan-Ru and PPh_3 of the one-pot conversion of FF to GVL at 160 °C for 30 h. Conditions: (a) 0.5 mmol FF in 1 mL ethanol, 3 mol-% chitosan-Ru, 8 mg of PPh_3, 200 mg of ZSM-5, 160 °C and 30 h; (b) 0.5 mmol FF in 1 mL ethanol, 3 mol-% chitosan-Ru, 8 mg of PPh_3, 5 equiv. 160 °C and 30 h; (c) 0.5 mmol FF in 1 mL ethanol, 3 mol-% chitosan-Ru, 200 mg of ZSM-5, 5 equiv. formic acid, 160 °C and 30 h; (d) 0.5 mmol FF in 1 mL ethanol, 200 mg of ZSM-5, 5 equiv. FA.

might be beneficial for the sufficient alcoholysis of FAL to EL due to its higher Brønsted acidity.

Under the optimized conditions, we also investigated the reaction kinetics of one-pot conversion of FF to GVL (Figure 3). It should be noted that FAL and 2-(Ethoxymethyl)furan (EMF) initially generated and then disappeared after being heated at 160 °C in less than 1 h, which indicated both the hydrogenation of FF to FAL and the alcoholysis of FAL to EL are rapid processes, consisting with the results as shown in Figure 2. After that, only EL is shown to be gradually transformed into GVL, this step proceeded relatively slow, thus being the rate-determining step of the one-pot conversion FF to GVL.

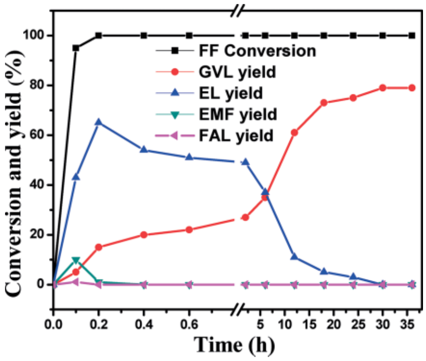


Figure 3. Kinetic behaviour of the one-pot production of GVL from FF. Reaction conditions: 0.5 mmol FF, 3 mol-% chitosan-Ru, 8 mg of PPh_3, 5 equiv. HCOOH, 200 mg of ZSM-5, 1 mL ethanol, 160 °C and 30 h.

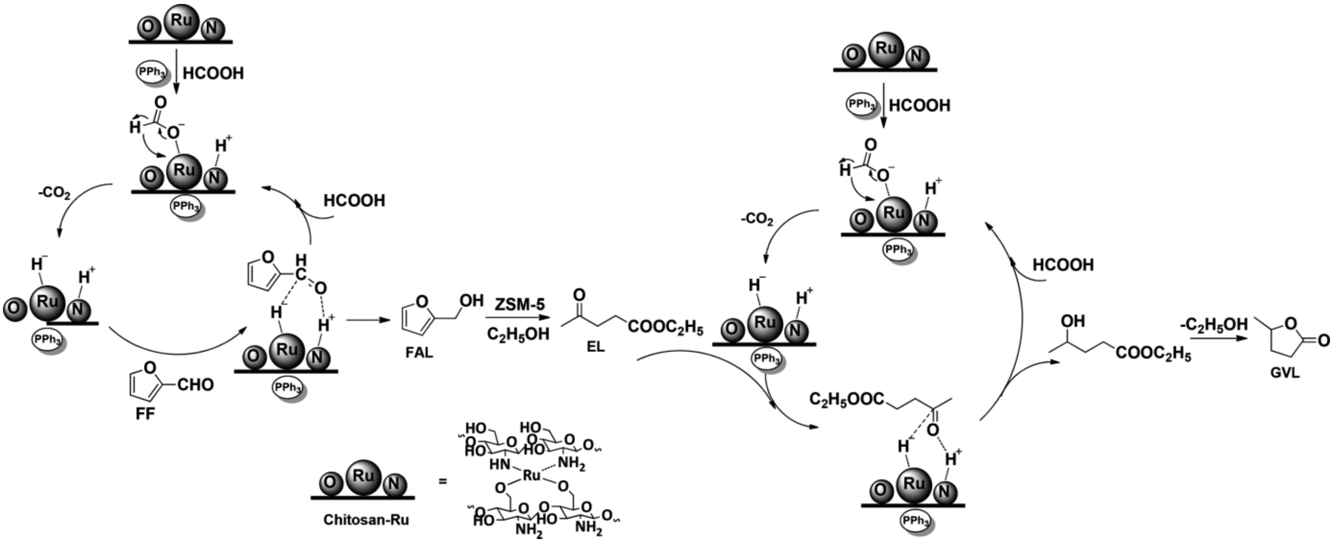
Current synthetic strategy employs LA or AL as the starting material for production of GVL, but generally LA needs to be highly purified. To reduce the production cost, it would be more desirable to directly synthesize GVL from one-pot transformation of abundant biomass resources such as xylose (the major intermediate produced during the hydrolysis of hemicellulose to FF) or hemicellulose (one of three important components in lignocellulosic biomass). Since the strong acidic ZSM-5 was previously reported for the degradation of xylan to FF,[37] we examined the effectiveness of chitosan/PPh_3/ZSM-5 system for the one-pot conversion of xylose and hemicellulose, and furnishing GVL in 26 % and 23 % yield after heated at 170 °C for 30 h, respectively (entries 5 and 7, Table 2). It is reported that the mixing of water with organic solvents is beneficial for the degradation of xylose and xylan to furfural.[38] Investigation towards the effects of water on the reaction showed that the addition of 10 equiv. of water led to a slightly enhanced GVL yield of 37 % and 30 % for xylose and hemicellulose, respectively (entries 6 and 8, Table 2). However, further increase of the amount of water showed no more improvements on the GVL yield.

Proposed Mechanism for the One-Pot Hydrogen Transfer of Furfural to GVL with Formic Acid (FA)

Based on the experimental details and previous literatures,[29b,29c,39] we proposed a possible reaction mechanism for the above-mentioned one-pot FF conversion to GVL (Scheme 2). It is noted that both Ru^{3+} ions and N atoms in the chitosan-Ru can serve as the possible active catalyst sites. During chitosan-Ru-catalyzed FF conversion to FAL in the presence of PPh_3, the electronegative N atoms acted as a base to adsorb FA to the catalyst surface. The H^+ of FA was captured and the $HCOO^-$ was coordinated with Ru^{3+} ions, which led to the generation of Ru-H^- species along with the release of CO_2. The reduction of C=O bonds in FF by both H^+ and Ru-H^- species resulted in the formation of FAL. The alcoholysis of FAL to EL catalyzed by ZSM-5 adopted the similar reaction pathway as reported in the previous mechanistic studies.[33] With the catalysis of chitosan-Ru, hydrogenation of the produced EL afforded 4-HPs, which was further converted to GVL through the lactonization.[16,40]

Recycle and Reuse Experiments

The recycle and reuse experiments were carried out to examine the economical and environment-friendly feature of chitosan-



Scheme 2. Proposed mechanism for the one-pot conversion of furfural into GVL with HCOOH as hydrogen source and ZSM-5 as connected catalyst.

Ru/PPh_3 catalyst system. After the completion of the reaction, catalysts were collected by filtration and washed by ethanol. After dried at 50 °C under vacuum for 5 h, the recovered catalysts were used for the next run. XPS spectra revealed that the recovered chitosan-Ru is similar with the fresh-prepared one (Figure 1b). In addition, ICP analysis indicated that there was only 0.04 % and 0.64 % metal weight percent decrease for FF to FAL and LA to GVL respectively in the recovered catalyst compared with the fresh-prepared catalyst (Table S1). Over 90 % yield of FAL could be achieved even after five runs of hydrogenation of FF by chitosan-Ru/PPh_3 (Figure 4a) while over 80 % GVL yield could be obtained after five runs of hydrogenation of LA by chitosan-Ru/PPh_3(Figure S2). These results confirmed the good recyclability of chitosan-Ru/PPh_3 catalyst system for both hydrogenation of FF to FAL and reduction of LA to GVL. For one-pot conversion of FF to GVL by chitosan-Ru/PPh_3/ZSM-5, GVL yield was drastically decreased to 49 % after five runs as Figure 4b, which might be ascribed to the gradual loss of chitosan-Ru catalyst during each recycle.

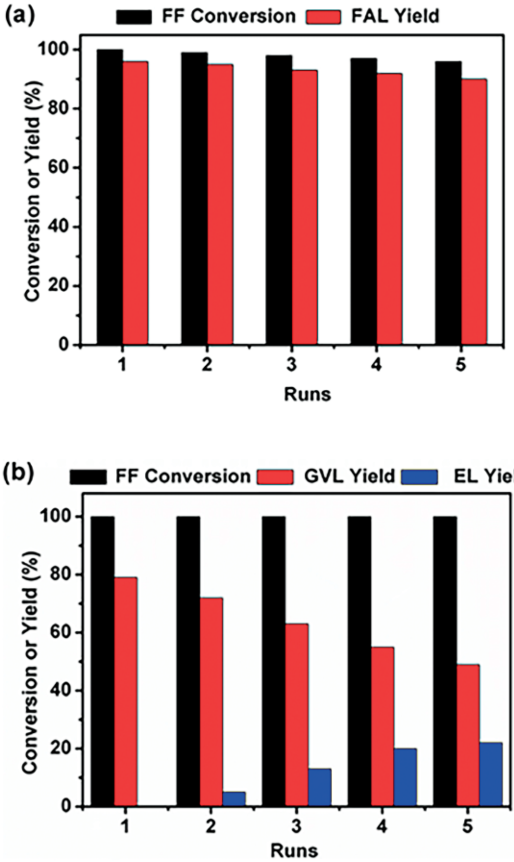


Figure 4. Recycle experiments for chitosan-Ru. (a) The catalyst reusability for the conversion of FF into FAL. Conditions: 0.5 mmol FF, 3 mol-% catalyst, 8 mg of PPh_3, 5 equiv. formic acid in 1 mL ethanol, 120 °C and 1.5 h. (b) The catalyst reusability for the conversion of FF into GVL. Conditions: 0.5 mmol FF, 3 mol-% catalyst, 8 mg of PPh_3, 200 mg of ZSM-5, 5 equiv. formic acid in 1 mL of ethanol, 160 °C and 30 h.

Conclusions

In summary, we developed a biomass-supported chitosan-Ru/PPh_3 catalyst system highly effective for both the hydrogenation of FF to FAL and reduction of LA or alkyl levulinate to GVL by using formic acid as green hydrogen source, achieving up to 99 % product yield under mild condition for both cases. The recycle and reuse experiments demonstrated the good recyclability of chitosan-Ru/PPh_3 system for both hydrogenation of FF and reduction of LA or alkyl levulinate. Moreover, the combination of acidic zeolite ZSM-5 with chitosan-Ru/PPh_3 could successfully realize a one-pot conversion of FF to GVL in up to 79 % yield. More importantly, this method enabled us to achieve a 37 % or 30 % yield of GVL from a one-pot catalytic transformation of xylose or hemicellulose respectively. These results should stimulate future efforts in developing highly effective catalyst system for the tandem conversion of the biomass-derived carbohydrates to GVL, thereby further expanding the application of GVL in future.

Experimental Section

Materials

Chitosan (medium viscosity, 98 %), xylose (98 %), ruthenium(III) chloride ($RuCl_3$, 99 %), palladium chloride ($PdCl_2$, 98 %), cobalt chloride ($CoCl_2$, 97 %), nickel chloride ($NiCl_2$, 97 %), furfural (FF, 98 %), furfuryl alcohol (FAL, 98 %), levulinic acid (LA, 98 %), ethyl levulinate (EL, 98 %), γ-valerolactone (GVL, 98 %), benzaldehyde (99 %), benzyl alcohol (99 %), anisaldehyde (98 %), anisalcohol (98 %), octanal (98 %), octanol (98 %), cinnamaldehyde (98 %), acetophenone (98 %), 1-phenylethanol (98 %) were purchased from Energy Chemical. Hemicellulose (reagent grade, 90 % xylan) was purchased from Sigma-Aldrich Chemical. Formic acid (HCOOH, 99 %), sodium formate (HCOONa, 98 %) and ammonia ($NH_3{\cdot}H_2O$, 28 %) were purchased from J&K company. H-type ZSM-5 (Si:Al = 25, 80, 200) (surface area: 340 m^2/g; pore size: 0.5 nm) were purchased from Nankai university catalyst Co., Ltd. Ethanol and other solvents were purchased from Adamas company and directly used without any purification.

Synthesis and Characterization of Chitosan-M Complexes (M = Ru, Pd, Co, Ni): Chitosan-M complexes were prepared according to a modified procedure.[26a] Taking chitosan-Ru as an example, chitosan (600 mg) and 100 mg of $RuCl_3$ was suspended in 20 mL of distilled water and the pH was adjusted and maintained between 9 or 10 by 28 % ammonia. After stirred overnight at room temperature (RT), the black solids were collected by filtration and washed by ethanol for three times, and then dried at 50 °C under vacuum for 5 h. The colourless filtrate indicated that most of ruthenium should be loaded onto chitosan. The other chitosan-M (M = Pd, Co, Ni) complexes were synthesized in the same manner as described for chitosan-Ru. The metal loading of chitosan-M was measured by ICP (inductively coupled plasma) carried out on a Perkin-Elmer Optima 3300 DV ICP instrument. Powder X-ray diffraction (PXRD) spectra of chitosan-M were examined on a Rigaku D/Max 2550 diffractometer using Cu-K_α radiation (λ = 1.5418 Å). Fourier transform infrared spectrometer spectrum (FT-IR) was recorded on Bruker VERTEX 80V in wavenumber range of 400-4000 cm^{-1} with the resolution ratio of 4 cm^{-1}. Thermal properties of chitosan and chitosan-M and the support chitosan were examined by thermogravimetry (TG) analysis on a TA Q50 instrument under N_2 atmosphere at a heating rate of 10 °C/min from room temperature to 800 °C. The NH_3 and CO_2-temperatured program desorption (NH_3/CO_2-TPD) were conducted on autochem II 2920 and the results was obtained from 50 °C to 200 °C, which was within the decomposition temperature of chitosan-Ru. X-ray Photoelectron Spectroscopy (XPS) characterization was performed on an ESCALAB 250 spectrometer, and the binding energies of the XPS spectra was referred to the C 1s (284.5 eV) as internal reference.

Catalytic Test

Hydrogenation of FF to FAL or LA to GVL with HCOOH: The reactions were carried out in a thick wall flask with Teflon-lined screw cap under air. Typically, 0.5 mmol FF was dissolved in 1 mL of THF in the flask, then 25 mg (3 mol-% relative to FF determined by ICP) chitosan-Ru, 8 mg of PPh$_3$ additive, and a certain amount of HCOOH were added into the flask. After heated at the desired temperature for measured time and cooled down to RT, the reaction mixture was analysed by GC with naphthalene as internal standard. Hydrogenation of LA and EL to GVL were carried out in the same manner as described for the hydrogenation of FF.

One-Pot Conversion of FF to GVL: Under N$_2$ atmosphere, 0.5 mmol FF was dissolved in ethanol in a thick wall flask, then (25 mg, 3 mol-%) chitosan-Ru, 8 mg of PPh$_3$ and 200 mg of ZSM-5 were added into the flask. After heated at 160 °C for 30 h and then cooled down to RT, the reaction mixture was measured by GC analysis with naphthalene as internal standard.

One-Pot Conversion of Xylose or Hemicellulose to GVL: The one-pot conversion of xylose or hemicellulose to GVL was carried out in the same manner as described for one-pot conversion of FF to GVL, replacing FF with 0.5 mmol xylose or hemicellulose. After heated at 170 °C for 30 h and then cooled down to RT, the reaction mixture was measured by GC analysis with naphthalene as internal standard.

Recycle and Reuse Experiments

After the reaction, the catalysts were collected by filtration and washed by ethanol for three times and dried under vacuum. The recovered catalyst was reused for the hydrogenation of FF with the supplement of 6 mol-% PPh$_3$ and the resulting reaction mixture was measured by GC analysis with naphthalene as internal standard. This process was repeated three times. The recycle and reuse experiments for the transformation of LA to GVL and one-pot conversion of FF to GVL were carried out in the same manner as described for the hydrogenation of FF to FAL.

Product Analysis

Conversion of substrates and product yield were measured by GC analysis performed on an Agilent 6890 system equipped with a flame ionization detector (FID) and a DB-WAX capillary column (15 m × 0.32 mm × 0.25 µm), using naphthalene as internal standard. The temperature of the injector and detector was set at 250 °C, and the oven was started at 60 °C, and was held for 5 min, raised to 70 °C at a rate of 5 °C/min and held for 10 min, then raised to 80 °C a rate of 2 °C/min and stayed for 4 min, at last, the temperature was continuously raised to 160 °C at the rate of 5 °C/min. Typical GC curves obtained for the one-pot conversion of FF to GVL was shown as Figure S4. ^{1}H NMR spectra were recorded on a Bruker Avance II 500 (500 MHz, ^{1}H) instrument at room temperature. Chemical shifts for ^{1}H spectra were referenced to internal solvent resonances and are reported as parts per million relative to SiMe$_4$.

Conflict of Interest

The authors declared no conflict of interest.

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Keywords: Biomass conversion · Furfural · Ruthenium · Supported catalysts · γ-Valerolactone

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Biomass Conversion

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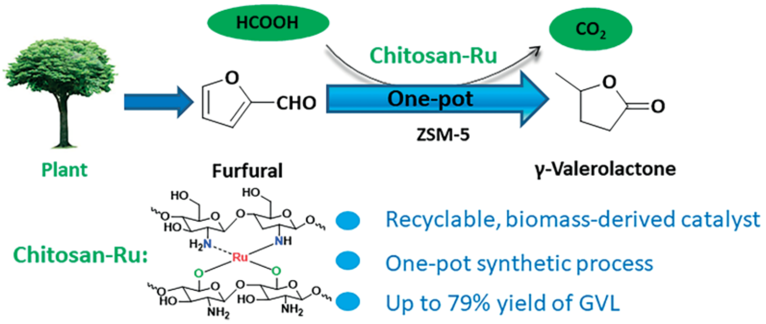
Production of γ-Valerolactone from One-Pot Transformation of Biomass-Derived Carbohydrates Over Chitosan-Supported Ruthenium Catalyst Combined with Zeolite ZSM-5



In the presence of formic acid, the combination of biomass-derived chitosan-Ru complex with zeolite ZSM-5 exhibited good performance towards the direct transformation of biomass such as furfural, xylose, and hemicellulose into γ-valerolactone.

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