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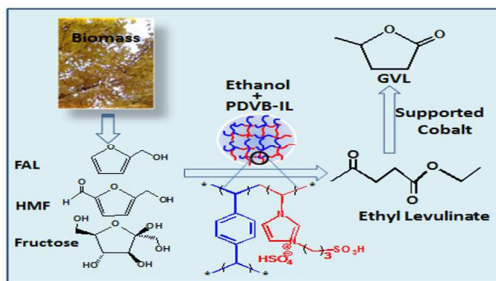
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Graphical abstract:



The PDVB-IL polymer and Co/TiO₂ is efficient and facilely recyclable for one-pot conversion of FAL, HMF, and fructose into GVL.

ARTICLE

One-pot conversion of carbohydrates into gamma-valerolactone catalyzed by highly cross-linked ionic liquid polymer and Co/TiO₂

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The acid catalytic conversion of carbohydrates into levulinic acid esters followed by the metal catalytic hydrogenation is an important approach to obtain gamma-valerolactone (GVL) from biomass. In this work, we prepared the highly cross-linked acid ionic liquid polymer (PDVB-IL) and the supported Co on TiO₂ (Co/TiO₂), which were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and elemental analysis. It was demonstrated that the PDVB-IL polymer could efficiently catalyze the esterification reaction of furfuryl alcohol (FAL), 5-hydroxymethylfurfural (HMF), and fructose with ethanol to produce the intermediate ethyl levulinate (EL), and the EL in the reaction mixture could be directly hydrogenated to GVL over the Co/TiO₂ without the need of purification, and high yields were obtained.

Introduction

Under the background of increasing demand for energy and limited reserves of traditional fossil resources on earth, exploring sustainable carbon source becomes a critical issue for human society.^{1, 2} Biomass is a well-accepted green and sustainable carbon source, which brings human light to overcome the above problem.³⁻⁵ Lignocellulose, consisting mainly of cellulose, hemicellulose, and lignin, is an abundant and renewable carbon source and can be biologically or chemically converted into various bulk chemicals, materials, and fuel additives.^{1, 6-13} One of the useful chemicals obtained from lignocellulose is gamma-valerolactone (GVL), which has wide applications including fuel additive, solvent, liquid fuel, and a precursor for the production of more valuable chemicals, etc.^{1, 14-19}

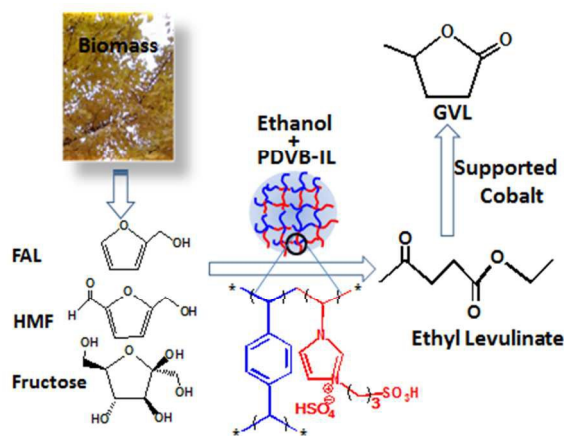
One of the approaches to obtain GVL from biomass is the C₅ sugar route with hemicellulose derived furfuryl alcohol (FAL) as the initial or intermediate molecule.^{1, 20} Tandem acid catalytic alcoholysis of FAL and subsequent metal catalytic hydrogenation reaction is a key process in this route.²¹⁻²³ Although the high efficiency of inorganic mineral acids, their corrosion and recovery problems drive researchers to investigate more economically and environmentally feasible heterogeneous acid catalysts. Lange et al. has proved that the strongly acidic resins and zeolites were effective catalysts for

the alcoholysis of FAL into ethyl levulinate (EL).²⁴ Zhang et al. developed a novel organic-inorganic hybrid solid acid catalyst for the conversion of FAL into alkyl levulinates.²⁵ Comparatively, the one-pot conversion directly from FAL to GVL is more attractive because no separation of the intermediate alkyl levulinates was needed. Rode et al. conducted the first attempt for the direct conversion of FAL to GVL by the combination of acid ILs and different supported noble metal catalysts.²⁰ The combination of acid resin Ambelyst-15 and RANEY® Ni was also reported to be efficient for the tandem conversion of FAL.¹⁸

Although much progress has been achieved as above stated, there are still many problems remaining to be solved for the direct conversion of FAL to GVL. For example, for the homogeneous catalysts, the most efficient catalyst reported up to date except the mineral acids is sulfonic acid functionalized ionic liquids. Its homogeneous property makes the recovery of the catalyst troublesome and consumption of large amounts of organic solvents, water, and energy.²⁰ For the reported heterogeneous catalysts, the humin by-products formed in the acid catalytic process could easily be adsorbed on the surface of the catalysts and deactivated them.²⁴⁻²⁶ The commonly used method to regenerate the catalysts is coke burn-off, while it is not suitable for the temperature-sensitive materials like resins.²⁴ Most of the reported metal catalysts were metal-based ones including the Ru, Rh, Pd, Ag, Ir, etc. The cost was high and the

reserve is very limited. The only reported non-noble metal was RANEY® Ni, but it required the purification of the intermediate EL.¹⁸ Obviously, more efforts are still desirable to improve the above aspects of the catalysts for GVL production.

Considering the above problems, in this work, we designed a novel catalytic system consisted of the highly cross-linked polymer of divinylbenzene with acid ionic liquid (PDVB-IL) and supported Co on TiO₂ (Co/TiO₂) for the one-pot conversion of FAL into GVL (Scheme 1), which consisted of esterification of the carbohydrates with ethanol to EL and hydrogenation reaction of EL to GVL. It was demonstrated that this catalytic system could catalyze the conversion of FAL, HMF, and fructose into GVL efficiently without the purification of the intermediate EL. The ILs could be recycled easily due to the heterogeneous property. The PDVB-IL polymer nearly did not adsorb humin, giving the catalyst a better reusability than that of the commercial Amberlyst-15.



Scheme 1 Schematic diagram of the tandem conversion of FAL, HMF, and fructose into GVL by the PDVB-IL polymer and supported cobalt catalytic system.

Experimental

Materials

Furfuryl alcohol (98%), 1-vinylimidazole (99%), silicon (IV) oxide (amorphous fumed, S.A. 130-170 m²/g), Amberlyst-15 (H) ion exchange resin, molecular sieve (zeolite Y, hydrogen), and celite (HyfloSupercel) were from Alfa Aesar®. Divinylbenzene (DVB, m- and p-mixture, 55% in EVB + DEB, stabilized with TBC), benzoyl peroxide (BPO, 98%), 1,4-butane sultone (99%), ethyl levulinate (98%), gamma-valerolactone (98%), and dodecane (99%) were purchased from J&K Chemical. Titanium (IV) oxide Aeroxide® P25 was from Acros Organics. Cobalt nitrate hexahydrate, sodium borohydride, MgO, ZrO₂, and other chemicals were A. R. grade and provided by Sinopharm Chemical Reagent Co. Ltd. H₂ (99.99%) was provided by Beijing Analytical Instrument Company.

Preparation of IL precursor

Sulfonic acid functionalized ionic liquid precursor was synthesized according to the reported procedures with modification.²⁰ In the

experiment, 5.40 g (40 mmol) 1,4-butane sultone and 0.94 g (10 mmol) 1-vinylimidazole were added into a 25 mL one-necked flask equipped with a magnetic stirrer. After reflux for 10 h at 70 °C under N₂ atmosphere with stirring, the reaction mixture was cooled down and solid product was recovered by filtration. The product was washed with diethyl ether to completely remove the unreacted reactants and then dried under vacuum overnight. A white zwitterion product was obtained with a yield of 98%. A stoichiometric amount of sulfonic acid was subsequently added dropwise to the zwitterions solution and the mixture was stirred at 80 °C for 6 h. After removal of water via evaporation, the viscous IL was obtained and dried under vacuum overnight. The prepared IL was confirmed by ¹H and ¹³C NMR. ¹H NMR (400 MHz, D₂O): δ 8.84 (s, 1H), 7.58 (s, 1H), 7.40 (s, 1H), 6.93 (dd, *J* = 15.6, 8.7 Hz, 1H), 5.59 (dd, *J* = 15.6, 2.7 Hz, 1H), 5.21 (dd, *J* = 8.7, 2.7 Hz, 1H), 4.08 (t, *J* = 7.1 Hz, 2H), 2.88 – 2.63 (m, 2H), 2.03 – 1.73 (m, 2H), 1.56 (dt, *J* = 18.3, 7.8 Hz, 2H). ¹³C NMR (100 MHz, D₂O): δ 134.30, 128.13, 122.72, 119.49, 109.25, 49.95, 49.18, 27.83, 20.82.

Preparation of the PDVB-IL polymer

The PDVB-IL polymer was prepared according to the previous method with modification.²⁷ The synthesized IL was copolymerized with DVB to form highly cross-linked polymer. In a typical polymerization, 0.34 g prepared IL, 1.40 g DVB, and 40 mL ethanol or ethanol/chloroform mixtures with different ratios were added into a 100 mL three-necked round flask and heated to 70 °C. The flask was purged with nitrogen and then 0.08 g benzoyl peroxide was added under stirring. The polymerization was allowed to proceed under N₂ atmosphere for 24 h. After cooling down, the product was separated by centrifugation, washed thoroughly with ethanol and water, and then dried under vacuum for use.

Preparation of supported cobalt

The supported cobalt was prepared by the impregnation and NaBH₄ reduction method.²⁰ In a typical procedure, 0.05 g support was suspended in a solution containing a calculated amount of Co(NO₃)₂•6H₂O under ultrasonication, and the mixture was stirred under room temperature for 2 h. Then 0.075 g NaBH₄ dissolved in 10 mL water was added dropwise and the system was stirred for half an hour. The supported cobalt was then separated via centrifugation, washed by ethanol, and kept in ethanol for use.

Catalyst characterization

The PDVB-IL polymer was characterized by scanning electron microscopy (SEM, HITACHI S-4800), Fourier transform infrared spectroscopy (FTIR, Bruker Tensor 27 spectrometer), and elemental analysis (EA, Flash EA 1112). The Co/TiO₂ was characterized by transmission electron microscopy (TEM, JEOL JEM-1011).

Reaction

For the conversion of FAL into EL, typically, 0.25 g (2.4 mmol) FAL, 0.18 g PDVB-IL polymer, and certain amount of ethanol were added into a 10 mL Teflon-lined stainless steel autoclave equipped with a magnetic stirrer. After removing the air via

vacuum pump, nitrogen of 1 atm was charged and the reactor was placed in a constant temperature oil bath of desired temperature. After reaction, the reactor was cooled in ice water and the organic phase was extracted from the mixture by ethyl acetate. The sample was analyzed by gas chromatograph (GC, HP 4890) equipped with a flame ionization detector (FID), and dodecane was used as the internal standard. Identification of the products and reactants was done using a GC-MS (SHIMADZU-QP2010) as well as by comparing the retention times to respective standards in GC traces. The results are expressed in mol% based on the total FAL loaded. In tandem reaction, the catalyst in each step was separated via centrifugation and washed once with ethanol for reuse. HMF and fructose were converted under the same procedures with FAL.

The activity of the supported cobalt was evaluated via the hydrogenation of EL. In a typical experiment, 1 g EL and 0.05 g of the prepared catalyst were introduced into the reactor. The reaction was conducted under 130°C and 3 MPa of hydrogen pressure. The product was analysed as stated above.

Results and Discussion

Preparation and characterization of the PDVB-IL polymer

The morphologies of the PDVB-IL polymer varied from dense microspheres to irregular porous gel, depending strongly on the solvent system (Fig. 1). The average sizes of the samples prepared in mixed solvents with ethanol/chloroform ratios (v/v) of 40:0, 30:10, and 20:20 were 360 nm, 500 nm, and 2.8 μm , respectively (Fig. 1a, 1b, and 1c). The change of morphology can be explained by the competition between the polymer chain growth rate and the phase separation rate.²⁷ Ethanol is a much poorer solvent for the polymer than chloroform. Once the polymer was formed, the phase separation occurred quickly, and the polymer shrunk and grew into the dense microsphere in ethanol, while this process was limited with the increasing of chloroform content, leading to the formation of larger aggregated spheres or irregular porous structure.

FTIR spectroscopy and elemental analysis were carried out to confirm the existence of IL segments in the polymer. As shown in Fig. 2, the peaks at 1654 cm^{-1} , 1174 cm^{-1} , and 1041 cm^{-1} attributed to C=N stretching vibrations of imidazole rings, asymmetrical and symmetrical stretching of SO_3 , respectively, appeared in the spectrum of the PDVB-IL polymer, proving the existence of IL structure.²⁷⁻²⁹ Elemental analysis showed the contents of IL segments increased with the increasing of chloroform contents (Fig. 3). This may be attributed to that higher chloroform concentration facilitated the diffusion of IL in the polymer matrix and enhanced the probability of the copolymerization of IL and DVB.²⁷ When the obtained polymers were used to convert FAL, the conversion of FAL decreased with the increasing of IL contents and the EL yield reached the highest value at the IL contents of ca. 3.1 wt% (Fig. 3). The decrease of the conversion of FAL may be attributed to that the slower phase separation rate at higher chloroform contents resulted in the embedment of more IL segments into

the matrix, leading to the decreasing of the accessibility of the acid sites.²⁷ Thus the PDVB-IL polymer prepared in ethanol/chloroform with ratio of 30:10 (v/v) was used to study the effects of reaction condition on the reaction.

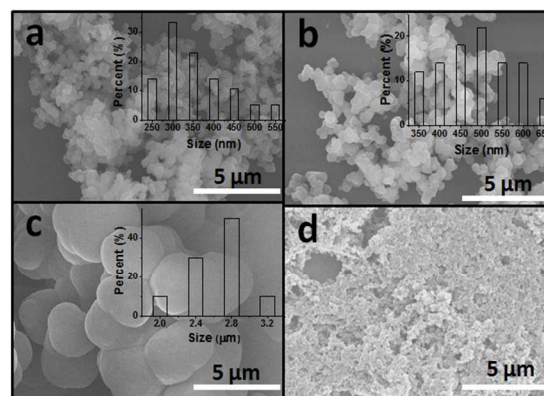


Fig. 1 SEM images and size distributions of the PDVB-IL polymer obtained in different solvents: neat ethanol (a), ethanol/chloroform mixtures with volume (mL) ratios of 30/10(b), 20/20(c), and 10/30(d).

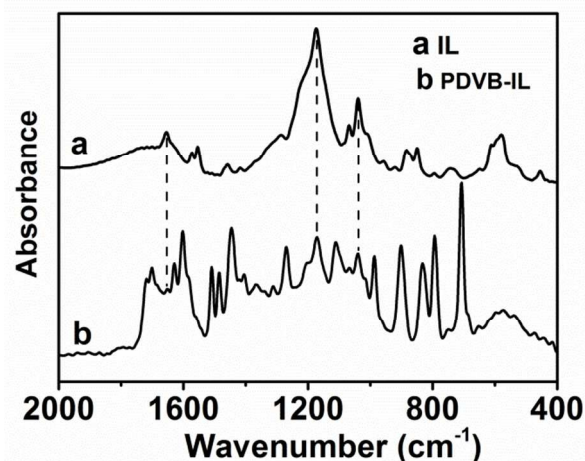


Fig. 2 FTIR spectra of the prepared IL and PDVB-IL polymer obtained in the ethanol/chloroform with volume ratio of 30/10.

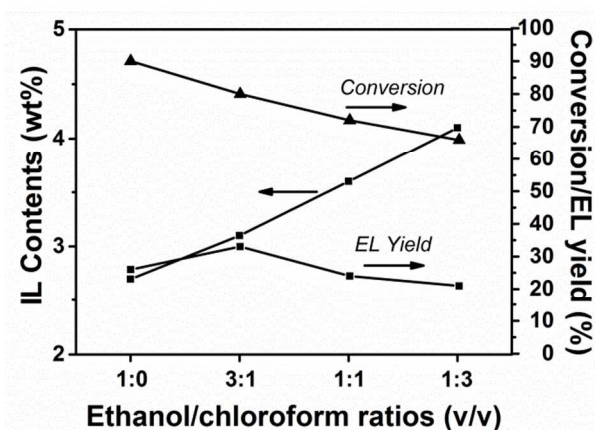


Fig. 3 The IL contents and activity of PDVB-IL polymers obtained under different ethanol/chloroform ratios. Reaction conditions: ethanol, 4 mL; FAL 0.25 g; PDVB-IL polymer, 0.18 g; N₂, 1 atm; 130 °C, 3 h.

Conversion of FAL and optimization

The effects of catalyst/substrate ratio, the amount of ethanol, the concentration of substrate, and temperature on the reaction were studied, and the results are presented in Fig. 4. It can be seen from Fig. 4a that increasing the catalyst/substrate mole ratio from 0.3% to 1.3% could significantly improve the EL yield from 14% to 38% within 12 h, while further increasing the catalyst/substrate ratio led to a slightly decrease in product yield, resulting from the fast formation of humin by-products. Increasing the volume of the solvent could improve the EL yield, while increasing the concentration of FAL at a constant solvent volume resulted in the decrease of the product yield (Fig. 4b and 4c), which was consistent with the previous report using other catalysts.²⁰ Temperature is also an important factor influencing the EL yield (Fig. 4d). A moderate EL yield of 33% was obtained even under 90 °C, and the yield increased up to 48% at the temperature of 130 °C. Further increasing the temperature to 150 °C resulted in the obvious drop in EL yield, which may be attributed to that the side reactions were also accelerated under higher temperature. Furthermore, in our experiments, we found that the only co-product was the intermediate methoxyfurfuryl alcohol formed by the reactant and ethanol only detected under lower temperature or shorter reaction time, and no other side-product except humin were detected.

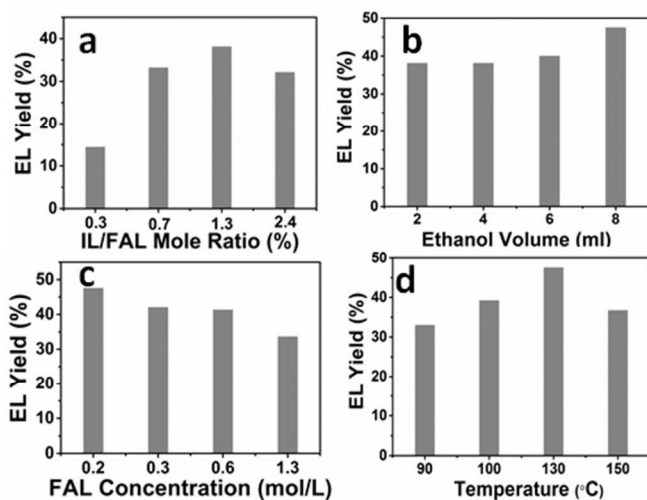


Fig. 4 Effects of the catalyst/substrate mole ratios (a), the volume of ethanol (b), the concentration of FAL (c), and temperature (d) on the EL yield. The catalyst/substrate mole ratios were the mole ratios of IL/FAL. Typical reaction conditions were as follows until otherwise stated in above figures: ethanol, 8 mL; FAL 0.12 g; PDVB-IL polymer, 0.18 g; N₂, 1 atm; 130°C, 12 h.

From above results, the formation of humin limited the further improvement of the EL yields. It has been reported that some organic solvents could inhibit the formation of humin to some extent.^{26, 30, 31} Thus, several common solvents were used, attempting to further improve the EL yields. The results were shown in Fig. 5. For all the cases, FAL was totally converted but with different EL yields. Unlike the reported results,^{30, 31} yields in acetonitrile and toluene were lower than that in pure ethanol, and yield in THF was similar to that in pure ethanol. Interestingly, the yield of the product in DMSO could reach 60% under the same conditions. During the experiments, we found that the intermediate ethoxy FAL was not totally converted into EL after reaction at 130 °C for 12 hours. Increasing the reaction time to 24 hours failed to fulfil the total conversion of the intermediate, while improving the reaction temperature to 150 °C succeeded in total conversion of the intermediate within 12 hours. The EL yield was increased to 75%, which was higher than the common solid acids.²⁴ As reported in literatures, DMSO could stabilize the furan structure in the reactants and suppress the condensation of the reactants and formation of by-products, thus improving the selectivity of EL.^{32,33}

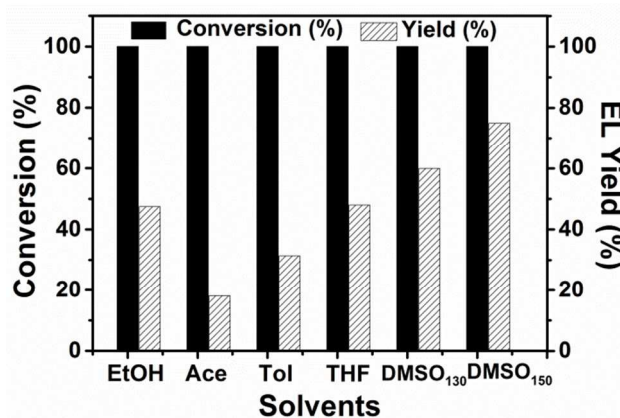


Fig. 5 Effects of solvents on the performance of the PDVB-IL polymer. EtOH, ethanol; Ace: acetonitrile; Tol, toluene; THF: tetrahydrofuran; DMSO: dimethyl sulfoxide. Reaction conditions: ethanol, 2 mL; solvent: 6 mL; FAL 0.12 g; PDVB-IL polymer, 0.18 g; N₂, 1 atm; 130 °C, 12 h. DMSO₁₃₀ and DMSO₁₅₀ means the reaction was conducted at 130 and 150 °C, respectively.

In our experiments, it is interesting to find that the PDVB-IL polymer nearly did not adsorb the humin by-products on its surface, compared with the commercial acid resins, such as Amberlyst-15. We detected the dry mass change of Amberlyst-15 and the PDVB-IL polymer, and found that a mass increase of ca. 5% after twice reactions occurred for Amberlyst-15 and no obvious mass change for the PDVB-IL polymer after reaction. The humin adsorption of the two catalysts could also be seen simply through the colour change after the reaction (Fig. 6a, 6b). The reusability comparison between our PDVB-IL polymer and Amberlyst-15 showed that the PDVB-IL polymer exhibited a better performance in both FAL conversion and EL

yield than that of Amberlyst-15 within 5 cycles (Fig. 6c). This indicated that the weak adsorption for humin is favourable to maintain the activity of the catalyst. We speculated that the strong adsorption of Amberlyst-15 for the humin could be related with its porous structures, which resulted in the accumulation of by-products. It is worth noting that the PDVB-IL polymer also suffered a decrease in activity at a speed slower than that of Amberlyst-15. The sulphur contents in the reaction solutions with pure ethanol as solvents without DMSO were detected. No obvious sulphur content was detected after the first catalysis reaction, while ca. 100 ppm of sulphur was detected after the fifth run. Thus we speculated that partial leaching of IL segments from the bulk polymer phase was the main reason for the activity decrease of the catalyst. We compared the FTIR spectra of the virgin and recycled PDVB-IL catalysts after used three times and no obvious differences were found, indicating that the main structures of PDVB-IL were well maintained after the reaction (Fig. 7).

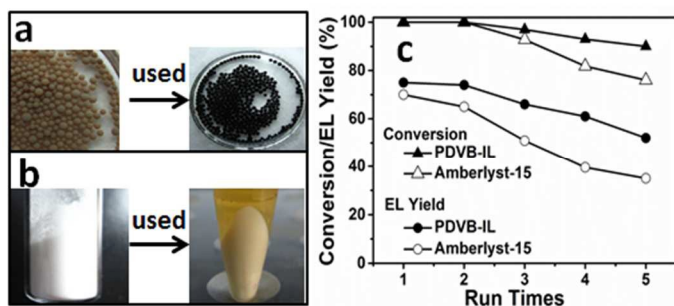


Fig. 6 Optical images of the Amberlyst-15 resin (a) and PDVB-IL polymer (b) before and after reaction and their reusability (c). The catalysts were washed once with ethanol before taking pictures. Reaction conditions: ethanol, 2 mL; DMSO, 6 mL; FAL, 0.12 g; PDVB-IL polymer, 0.18 g or Amberlyst-15, 0.2 g; N₂, 1 atm; 130 °C; 12 h. The catalysts were washed once with ethanol before the next run.

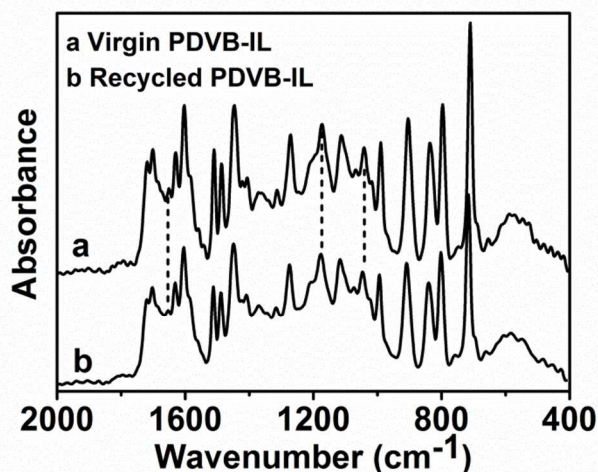


Fig. 7 Comparison of FTIR spectra of the virgin and recycled PDVB-IL catalysts after used three times.

One-pot conversion of carbohydrates into GVL

After optimizing the reaction conditions of the PDVB-IL polymer for catalytic conversion of FAL into EL, we conducted the one-pot conversion of FAL into GVL. The supported cobalt was attempted for the first time in the conversion of FAL into GVL. The impregnation and NaBH₄ reduction method was used to load cobalt on various materials, and the hydrogenation of EL to GVL was used to evaluate the activity (Table 1). Among the materials investigated, TiO₂ gave the highest GVL yield (entry 8). Increasing the loading of cobalt on TiO₂ could significantly increase the GVL yield (entries 8–10). TEM characterization of Co/TiO₂ (20 wt% Co) showed that the Co particles with a diameter of 50–150 nm were dispersed uniformly in the TiO₂ matrix without obvious aggregation (Fig. 8).

The tandem conversion of FAL into GVL was shown in the diagram in Table 2. It can be seen that the catalytic system is very efficient in the conversion of FAL with the intermediate EL yield of 75% and the final GVL yield up to 69%, which was even higher than that of the combination of noble Ru/C and [BMIm-SH][HSO₄].²⁰ The activity maintained well in the second run (entries 1–2). A decrease in the GVL yield was observed since the third recycle (entries 3–6). We detected the cobalt contents in the reaction solutions. No obvious cobalt was found after the first two recycles, but a content of ca. 70 ppm was detected after the fifth run. Thus the deactivation of the catalytic system may be attributed to the leaching of IL segments, as analysis above, and subsequent partial cobalt dissolution. We expanded our catalytic system to the conversion of other carbohydrates, including HMF and fructose (entries 7–8), and GVL yields of 62% and 55% were obtained, respectively, which were comparable to the reported results using Amberlyst-15 and RANEY[®] Ni as the catalyst system.¹⁸

Considering the raw carbohydrate may come from the aqueous systems, we further investigated the effect of water on our catalytic system. The results showed that serious coking and no obvious products were detected in pure water due to the instability of FAL in water. Thus we turned to the mixture of water and ethanol/DMSO and found that a water content of 10% (v/v) had no obvious influence on the high EL and GVL yields.

Table 1 Screening of the supports for cobalt immobilization^a

Entry	Supports	Conversion/%	Selectivity/%	Yield/%
1	Control	8	84.3	6.8
2	MgO	16.8	94.1	15.8
3	ZrO ₂	31	94.4	29.2
4	Zeolite	14.1	94.6	13.3
5	SiO ₂	15.7	94.1	14.8
6	Amberlyst-15	22.8	70.4	16
7	Celite	35.2	97.9	34.5
8	TiO ₂	45.2	92.1	41.7
9	TiO ₂ ^b	64.9	91.0	59.1
10	TiO ₂ ^c	78.8	91.8	72.3

^aTypical reaction conditions: EL, 1.0 g; supported cobalt (5 wt%), 0.05 g; H₂, 3 MPa; 130 °C; 3 h. ^bCobalt loading: 10 wt%; ^cCobalt loading: 20 wt%.

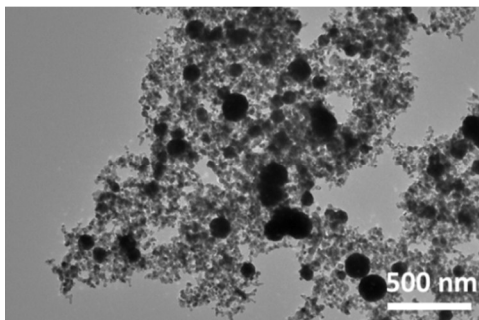


Fig.8 TEM image of Co/TiO₂ with a Co loading of 20 wt%.

Table 2 One-pot conversion of carbohydrates into GVL in the PDVB-IL polymer and Co/TiO₂ catalyst system^a

Entry	Substrate	Conversion/%	EL Yield/%	GVL Yield/%
1 ^b	FAL	>99	75	69
2 ^b	FAL	>99	74	66
3 ^b	FAL	97	66	56
4 ^b	FAL	93	61	48
5 ^b	FAL	90	52	33
6 ^b	FAL	70	35	18
7	HMF	>99	73	62 ^c
8	Fructose	>99	65	55

^aReaction conditions: the first step, 1 mmol carbohydrate (FAL, HMF, or fructose); 0.18 g PDVB-IL polymer; 2 mL ethanol, 6 mL DMSO; N₂, 1 atm; 150 °C; 12 hours. In the second step, Co/TiO₂ 0.05 g; H₂, 3 MPa; 130°C; 6 hours. Yields were all given as the mole percent of the initiate substrates. ^b Entries 1—6, reusability of the catalytic systems for FAL: run times 1—6; ^c 24 hours for the hydrogenation reaction.

Conclusions

In this work, we have developed an efficient catalytic system consisting of the PDVB-IL polymer and Co/TiO₂ for the one-pot conversion of FAL, HMF, and fructose into GVL via EL. Under the optimized conditions, the yields of GVL can reach 69%, 62%, and 55% from FAL, HMF, and fructose, respectively. The PDVB-IL polymer is facile to recycle due to the heterogeneous property, and its reusability is better than that of acid resins (Amberlyst-15) due to the weak adsorption for humin. The obvious advantages of this catalytic system, including high efficiency, facile recovery, and use of low-cost and abundant cobalt as metal catalysts, make it a promising candidate in biomass utilization.

Acknowledgements

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Notes and references

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