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ARTICLE

Industrially scalable and cost-effective synthesis of 1,3-cyclopentanediol with furfuryl alcohol from lignocellulose

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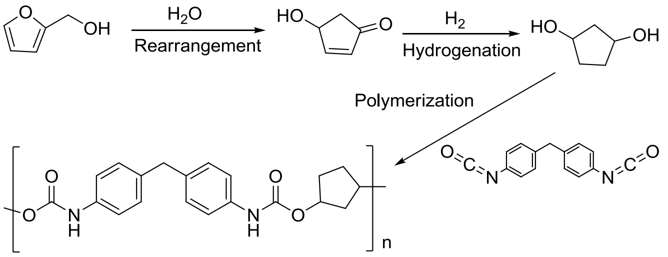
A new route for the selective synthesis of renewable 1,3-cyclopentanediol was developed by the aqueous phase rearrangement of furfuryl alcohol to 4-hydroxycyclopent-2-enone followed by hydrogenation. The presence of small amount of base catalysts is benefical for the aqueous phase rearrangement of furfuryl alcohol to 4-hydroxycyclopent-2-enone. Such a promotion effect of base catalysts can be rationalized by restraining the gneration of levulinic acid which may catalyze the polymerization of furfuryl alcohol. In the hydrogenation of 4-hydroxycyclopent-2-enone to 1,3-cyclopentanediol, evident solvent effect was noticed. Higher carbon yields of 1,3-cyclopentanediol were obtained when tetrahydrofuran was used as the solvent. In the large scale tests with high initial concentrations of feedstocks, high overall carbon yield (72.0%) of 1,3-cyclopentanediol was achieved over cheap catalysts (MgAl-HT and Raney Ni). As a potential application, the 1,3-cyclopentanediol as obtained was successfully used as a monomer in the synthesis of polyurethane.

Introduction

Due to the increase of social concern about energy and environmental problems, the catalytic conversion of renewable, inedible and abundant lignocellulose to fuels[1] and value-added chemicals[2] has drawn tremendous attention. Compared with fossil energy, lignocellulose is richer in oxygenic groups. Therefore, the selective conversion of lignocellulose to high value oxygenates has great significance. Diols are a family of monomers which are widely used in the polymer industry. During the past years, several routes have been developed for the selective synthesis of renewable linear diols (such as ethylene glycol,[3] 1,2-propanediol,[4] 1,3-propanediol,[5] 1,4-butanediol,[6] 1,5-pentanediol,[7] 1,6-hexanediol,[8] *etc.*) with lignocellulose or its derivates. So far, there is no report about the synthesis of renewable cyclic diols.

1,3-Cyclopentanediol is a cyclic diol which can be used in the production of polyester, polyether and polyurethane. Currently, 1,3-cyclopentanediol is usually produced from the cyclopentadiene in non-renewable fossil resources.[9] The synthesis processes to 1,3-cyclopentanediol also involves the utilization of some environmental unfriendly reagents (such as diborane, halogenated agents, peroxide reagents, *etc.*). From the pointview of sustainable development and environmental protection, some environmental friendly technologies for the production of 1,3-cyclopentanediol with renewable feedstocks should be developed.

Furfuryl alcohol is the selective hydrogenation product of furfural which has been manufactured in industrial scale with the hemicellulose part of agriculture waste and forest residues. In this work, a new route was developed for the synthesis of renewable 1,3-cyclopentanediol (see Scheme 1) by the aqueous phase rearrangement of furfuryl alcohol, followed by hydrogenation. To the best of our knowledge, this is the first report on the selective synthesis of cyclic diol from a lignocellusic platform chemical. As a potential application, we also explored the possibility to use the 1,3-cyclopentanediol as obtained in the synthesis of polyurethane.



Scheme 1. Reaction pathway for the synthesis of partially renewable polyurethane with furfuryl alcohol.

Experimental

Preparation of catalyst

NaOH, Na_2CO_3, CaO, MgO and CeO_2 were supplied by Sinopharm Chemical Reagent Co. Ltd. Bis(lauroyloxy)dibutylstannan, Ru/C (Ru content: 5.0wt.%) and Pd/C (Pd content: 5.0wt.%) were purchased from Aladdin Industrial Corporation.

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Raney Ni was provided by Dalian General Chemical Industry Co., Ltd. MgAl hydrotalcite (MgAl-HT) catalyst was prepared by the conventional co-precipitation method described in literature.[10] In brief, 50 mL aqueous solution containing 9.60 g $Mg(NO_3)_2{\cdot}6H_2O$ and 4.68 g $Al(NO_3)_3{\cdot}9H_2O$ (at a Mg/Al atomic ratio of 3:1) was added drop-wise into another 50 mL aqueous solution containing 4.24 g Na_2CO_3 and 2.40 g NaOH under vigorous stirring. The pH value of the mixture was adjusted to 10 with an aqueous solution of NaOH (3 mol L^{-1}). The suspension was kept at 338 K for 18 h to get a precipitate with hydrotalcite-like structure. The product was filtrated, repeatedly washed with deionized water and dried at 353 K for 8 h. Before being used for the aqueous phase arrangement of furfuryl alcohol, the MgAl-HT catalyst was calcined in nitrogen flow at 773 K for 4 h.

Activity tests

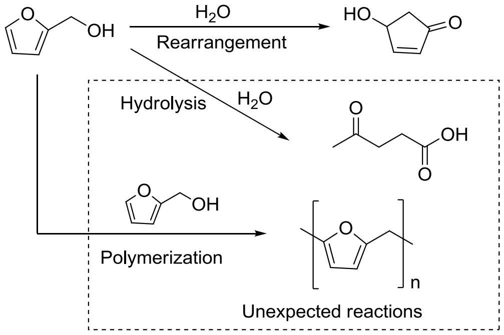
Aqueous phase rearrangement of furfuryl alcohol. The aqueous phase rearrangement of furfuryl alcohol was carried out in a semi-continuous reaction system. After the loading of catalyst and 40 mL water, the stainless-steel autoclave (Parr Instrument Co., 100 mL) was purged with Ar for six times. The reactor was heated to the set temperature. Then, 10 mL aqueous solution (10wt.%) of furfuryl alcohol (Sinopharm Chemical Reagent Co. Ltd.) was injected into the reactor with a HPLC pump (Elite P230, injection time: 1 min). The reactant solution was stirred at rate of 800 rpm for specific time. For comparison, a conventional batch reactor was also employed to conduct the reaction. In that case, water and furfuryl alcohol were added to the reactor simultaneously and then heated to target temperature. The reaction was carried out at 513 K in Ar atmosphere under stirring at rate of 800 rpm. After the tests, the reactor was quenched to room temperature by cool water. The liquid products were taken out from the reactor, centrifuged and analyzed with an Agilent 1200 HPLC equipped with a Shodex Sugar SC1011 column and a refractive index detector.

Hydrogenation of 4-hydroxycyclopent-2-enone. The hydrogenation of 4-hydroxycyclopent-2-enone was performed in a 100 mL Parr 4848 reactor at 5 MPa H_2 for 1 h. The detail information for preparation of 4-hydroxycyclopent-2-enone was described in supporting information. For each test, 0.1 g catalyst, 0.7 g 4-hydroxycyclopent-2-enone and 40 g solvent were used. The liquid products were analyzed by an Agilent 6890N GC equipped with a HP-INWAX capillary column (30 m, 0.32 mm ID, 0.1 μm film) and a FID detector.

Results and discussion

Aqueous phase rearrangement of furfuryl alcohol

In the first part of this work, we studied the aqueous phase rearrangement of furfuryl alcohol to 4-hydroxycyclopent-2-enone. As what has been observed by Hronec *et. al.* in their previous work,[11] the rearrangement of furfuryl alcohol can take place in pure water without using any catalyst. However, according to our analysis, a 4-hydroxycyclopent-2-enone carbon yield of only 36.4% was obtained at 513 K. At the same time, we also noticed the generation of yellowish-brown coloured solid product during the reaction. This result can be explained by the polymerization of furfuryl alcohol, which may compete with its rearrangement to 4-hydroxycyclopent-2-enone. To minimize the polymerization of furfuryl alcohol during the heating of reactant to the target temperature, we injected the 10 wt.% furfuryl alcohol solution (by HPLC pump) into water which was pre-heated and stirred in batch reactor at 513 K. As we expected, a higher carbon yield (53.5%) of 4-hydroxycyclopent-2-enone was obtained by the direct addition of furfuryl alcohol to the reaction system at 513 K. Besides 4-hydroxycyclopent-2-enone, levulinic acid (carbon yield: 13.3%) was also identified in the aqueous product (see Figure S1 and Figure S2 for the HPLC chromatogram and NMR spectra of liquid products). According to the literature,[12] levulinic acid is produced by the hydrolysis of furfuryl alcohol (see Scheme 2). This compound may act as an acid catalyst to promote the polymerization of furfuryl alcohol.[13]



Scheme 2. Reaction pathway for the generation of 4-hydroxycyclopent-2-enone, levulinic acid and polymer during the aqueous phase rearrangement of furfuryl alcohol.

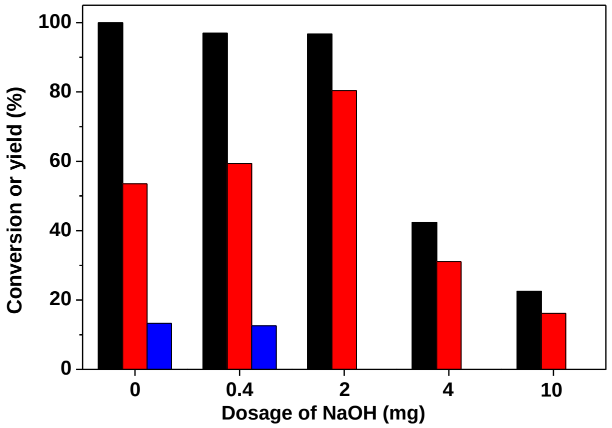


Figure 1. Furfuryl alcohol conversion (black bars) and the carbon yields of 4-hydroxycyclopent-2-enone (red bars) and levulinic acid (blue bars) as the function of NaOH dosage. Reaction conditions: 513 K, 1 min; 10.0 g 10wt.% aqueous solution of furfuryl alcohol and 40 g water were used for each test.

After introducing small amounts of NaOH into the reaction system, the carbon yield of 4-hydroxycyclopent-2-enone was further improved (see Figure 1). The presence of NaOH also led to the decrease in the carbon yield of levulinic acid. Based on this phenomenon, the promotion effect of NaOH can be

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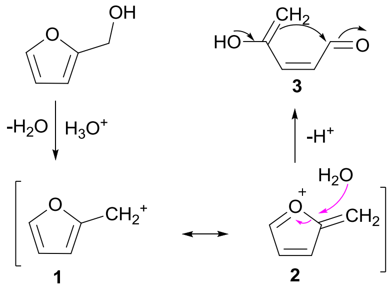
rationalized by restraining the hydrolysis of furfuryl alcohol (or the formation of levulinic acid). As we can see from Figure 1, there is an optimum value for the dosage of NaOH (2 mg for the investigated system). Further increase of NaOH dosage above 2 mg results in lower furfuryl alcohol conversion and the decrease of 4-hydroxycyclopent-2-enone carbon yield. This phenomenon may be explained because the aqueous phase rearrangement of furfuryl alcohol to 4-hydroxycyclopent-2-enone is also an acid catalysed reaction (see Scheme 3 for the reaction mechanism suggested in literature[11, 14]). Compared to the hydrolysis (or polymerization) of furfuryl alcohol, this reaction is less sensitive to the restraining effect of base under the investigated conditions.



Scheme 3. Reaction mechanism for the aqueous phase rearrangement of furfuryl alcohol to 4-hydroxycyclopent-2-enone.[11, 14]

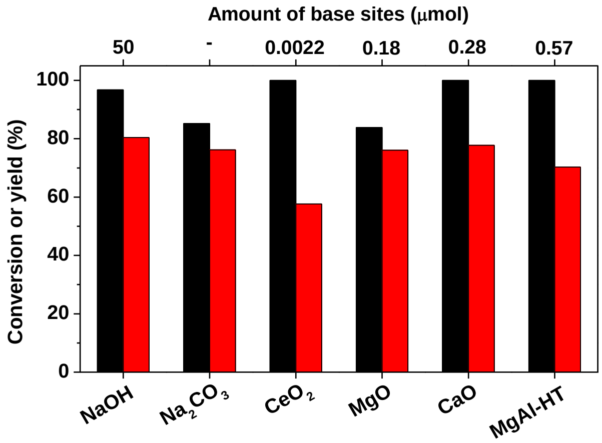


Figure 2. Furfuryl alcohol conversions (black bars) and the carbon yields of hydroxycyclopent-2-enone (red bars) over different catalysts. Reaction conditions: 513 K, 1 min; 10.0 g 10wt.% aqueous solution of furfuryl alcohol, 40 g water and 2 mg catalyst were used for each test. The amounts of base sites on solid base catalysts were calculated according to CO_2-TPD results.

The promotion effect of sodium hydroxide is not unique. As we can see from Figure 2, the presence of other often used base catalysts (such as Na_2CO_3, CaO, MgO, MgAl-hydrotalcite (MgAl-HT) and CeO_2) favours the aqueous phase rearrangement of furfuryl alcohol to 4-hydroxycyclopent-2-enone. Taking MgAl-HT for example, a high carbon yield (82.7%) of hydroxycyclopent-2-enone can be achieved over this catalyst under the optimum reaction conditions (5 mg MgAl-HT, 503 K, 2 min; see Figure S3-S5 in supporting information).

4-Hydroxycyclopent-2-enone is an important intermediate for the synthesis of natural products and analogues.[15] Due to the polymerization of furfuryl alcohol, it is challenging to achieve high carbon yield of 4-hydroxycyclopent-2-enone from the aqueous phase rearrangement of furfuryl alcohol. During the past years, great efforts have been devoted to improve the selectivity of 4-hydroxycyclopent-2-enone. For example, Reiser *et al.*[14] found that high carbon yields of 4-hydroxycyclopent-2-enone can be achieved by microwave irradiation (80%) or microreactor (87%) with the assistance of toluene. Analogously, Fadnavis *et al.* also studied the aqueous phase rearrangement of furfuryl alcohol to 4-hydroxycyclopent-2-enone in a microreactor.[16] It was found that the addition of N-methylpyrrolidinone as a co-solvent can greatly restrain the polymer formation. Under the optimized conditions, a high carbon yield (up to 98%) of 4-hydroxycyclopent-2-enone was obtained. The detail information about the above processes was given in Table S1 in support information. Compared with these methods, the new method developed in this work has two obvious advantages: 1) Conventional reactor and heating mode were used. This is suitable for the large-scale synthesis 4-hydroxycyclopent-2-enone. 2) Water was used as the only solvent in this reaction, which made the subsequent product separation more convenient, economic and environmental friendly. Such an advantage is more evident when we used solid base as the catalyst.

Hydrogenation of 4-hydroxycyclopent-2-enone

Subsequently, we studied the hydrogenation of 4-hydroxycyclopent-2-enone over the Raney Ni, Ru/C and Pd/C catalysts. According to our analysis, 3-hydroxycyclopentanone was identified as the main product from the aqueous phase hydrogenation of 4-hydroxycyclopent-2-enone at room temperature (see Figure S6 for the NMR spectra of 3-hydroxycyclopentanone). From this result, we can see that the hydrogenation of C=C bond in 4-hydroxycyclopent-2-enone molecule is easier than that of C=O bond. The 3-hydroxycyclopentanone as obtained can be used as a building block in the synthesis of renewable jet fuel. In some recent literatures,[17] a series of jet fuel range cycloalkanes with high density (0.82-0.87 g mL^{-1}) have been synthesized by the hydroxyalkylation/alkylation (or aldol condensation) of cyclopentanone followed by hydrodeoxygenation. Compared to the Ru/C catalyst, the Pd/C and Raney Ni catalysts are more active for the hydrogenation of 4-hydroxycyclopent-2-enone (see Figure 3). Over them, high carbon yields of 3-hydroxycyclopentanone (~80%) were achieved after the reaction was carried out at 293 K for 1 h. This result is consistent with what has been obtained by Ulbrich (82.3%) over Pt and Pd catalysts under similar reaction conditions (see Table S2 in supporting information).[18]

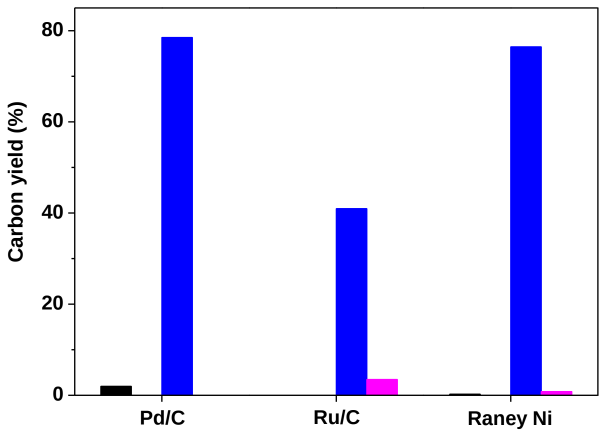


Figure 3. Carbon yields of cyclopentanone (black bars), cyclopentanol (red bars), 3-hydroxycyclopentanone (blue bars) and 1,3-cyclopentanediol (magenta bars) from the aqueous phase hydrogenation of 4-hydroxycyclopent-2-enone. Reaction conditions: 293 K, 5 MPa H_2, 1 h; 0.1 g catalyst, 0.7 g 4-hydroxycyclopent-2-enone and 40 g H_2O were used for each test.

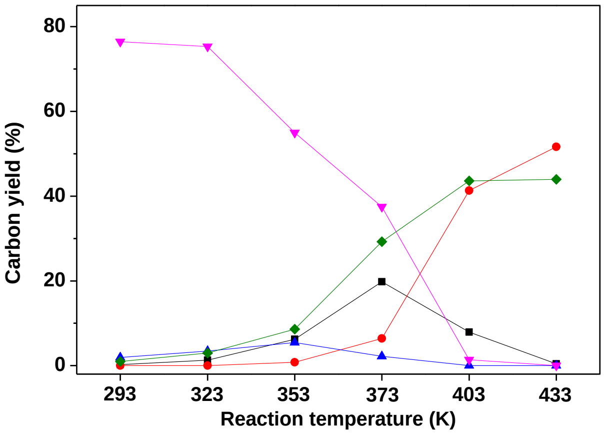


Figure 4. Carbon yields of cyclopentanone (■), cyclopentanol (●), cyclopent-3-enone (▲), 3-hydroxycyclopentanone (▼), and 1,3-cyclopentanediol (♦) as the function of reaction temperature. Reaction conditions: 5 MPa H_2, 1 h; 0.1 g Raney Ni, 0.7 g 4-hydroxycyclopent-2-enone and 40 g H_2O were used for each test.

With the increasing of reaction temperature, the 3-hydroxycyclopentanone was further hydrogenated to 1,3-cyclopentanediol (see Figure 4). However, this reaction is accompanied by the dehydration and hydrogenation of 3-hydroxycyclopentanone to cyclopentanone and cyclopentanol. After the hydrogenation of 4-hydroxycyclopent-2-enone was carried out at 433 K for 1 h (see Figure 5), the carbon yields of 1,3-cyclopentanediol over Raney Ni and Ru/C were 44.0% and 32.0%, respectively. In contrast, the carbon yield of 1,3-cyclopentanediol over the Pd/C catalyst is almost zero. This phenomenon can be explained by the C=C bond being easier to hydrogenate than the C=O over Pd-based catalysts.[19] As we can see from Scheme 4, the dehydration of 3-hydroxycyclopentanone will lead to the generation of an α,β-unsaturated ketone with high stability (conjugative effect), which may be the reason for the low carbon yields of 1,3-cyclopentanediol obtained in some recent studies[20] about the aqueous phase hydrogenation of furfural and furfuryl alcohol.

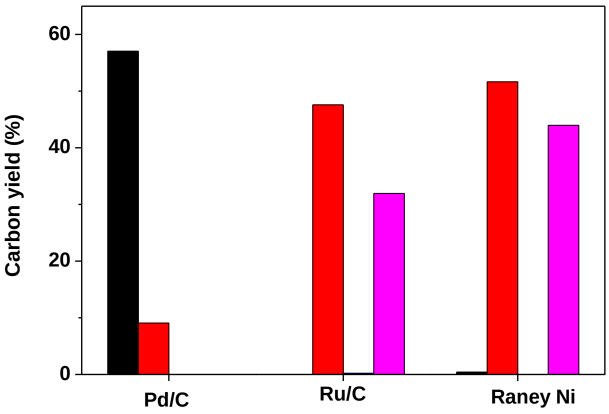
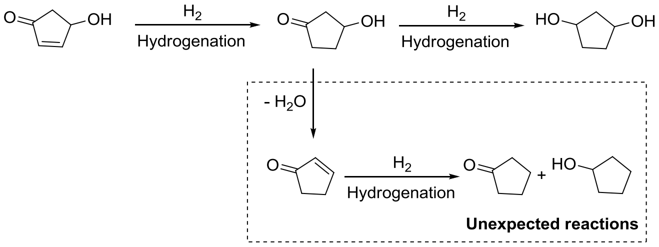


Figure 5. Carbon yields of cyclopentanone (black bars), cyclopentanol (red bars), 3-hydroxycyclopentanone (blue bars) and 1,3-cyclopentanediol (magenta bars) from the aqueous phase hydrogenation of 4-hydroxycyclopent-2-enone. Reaction conditions: 433 K, 5 MPa H_2, 1 h; 0.1 g catalyst, 0.7 g 4-hydroxycyclopent-2-enone and 40 g H_2O were used for each test.



Scheme 4. Reaction pathways for the production of 3-hydroxycyclopentanone, 1,3-cyclopentanediol, cyclopent-3-enone, cyclopentanone and cyclopentanol from the hydrogenation of 4-hydroxycyclopent-2-enone.

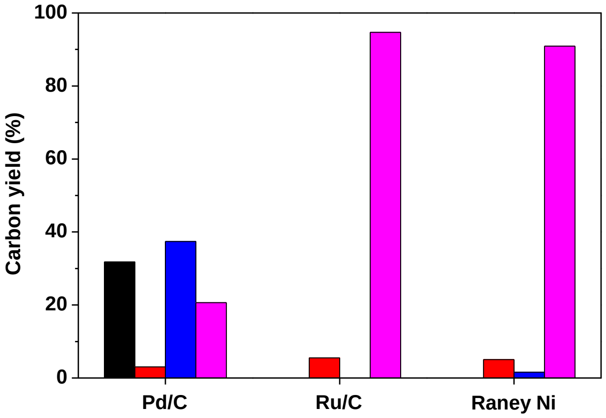


Figure 6. Carbon yields of cyclopentanone (black bars), cyclopentanol (red bars), 3-hydroxycyclopentanone (blue bars) and 1,3-cyclopentanediol (magenta bars) from the liquid phase hydrogenation of 4-hydroxycyclopent-2-enone over different catalysts. Reaction conditions: 433 K, 5 MPa H_2, 1 h; 0.1 g catalyst, 0.7 g 4-hydroxycyclopent-2-enone and 40 g tetrahydrofuran were used for each test.

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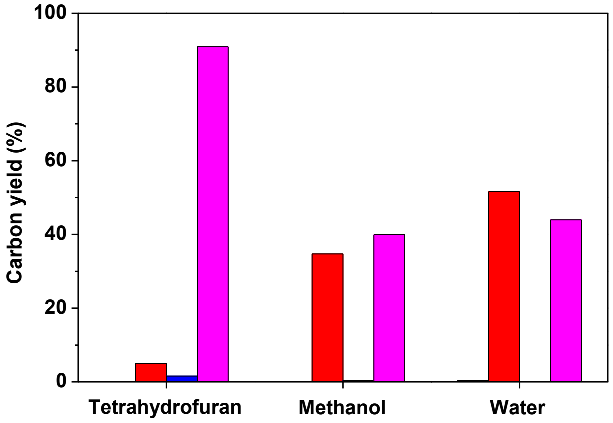

Figure 7. Effect of solvent on the carbon yields of cyclopentanone (black bars), cyclopentanol (red bars), 3-hydroxycyclopentanone (blue bars) and 1,3-cyclopentanediol (magenta bars) over the Raney Ni catalyst. Reaction conditions: 433 K, 5 MPa H_2, 1 h; 0.1 g catalyst; 0.7 g 4-hydroxycyclopent-2-enone and 40 g solvent were used for each test.

It is very interesting that high carbon yields of 1,3-cyclopentanediol can be achieved by the hydrogenation of 4-hydroxycyclopent-2-enone over the Ru/C (94.7%) and Raney Ni (90.9%) catalysts (see Figure 6) when tetrahydrofuran was used as the solvent (the NMR spectra of the 1,3-cyclopentanediol were illustrated in Figure S7 and Figure S8 in supporting information). However, such a promotion effect is not observed for other organic solvent (such as methanol) (see Figure 7). Taking into consideration of the lower price and higher availability of Ni than those of Ru, we believe that the Raney Ni is a promising catalyst in real application. In our future work, more efforts will be made to understand the intrinsic reason for the unique promotion of tetrahydrofuran.

To explore the possibility for real application, we also investigated the aqueous phase rearrangement of furfuryl alcohol and the subsequent 4-hydroxycyclopent-2-enone hydrogenation with a one-gallon batch reactor at higher initial substrate concentrations. From the results shown in Table 1, the carbon yield of 4-hydroxycyclopent-2-enone only slightly decreased (from 82.7% to 77.6%) after we synchronously increased the reaction scale and the initial concentration of furfuryl alcohol solution (from 10wt.% to 20wt.%). However, the further increase of the initial furfuryl alcohol concentration from 20wt.% to 40wt.% led to the evidently decrease of 4-hydroxycyclopent-2-enone carbon yield from 77.6% to 67.1%. This phenomenon can be rationalized because the higher initial furfuryl alcohol concentration in feedstock is favourable for its polymerization. Based on an overall consideration of efficiency and selectivity, we hypothesize that 20wt.% may be the optimum initial substrate concentration for the aqueous phase rearrangement furfuryl alcohol. By the hydrogenation of 15.8wt.% tetrahydrofuran solution of 4-hydroxycyclopent-2-enone at larger scale (see Table S3 in supporting information), 92.8% carbon yield of 1,3-cyclopentanediol was obtained.

Table 1. Furfuryl alcohol conversion and the carbon yield of 4-hydroxycyclopent-2-enone from the aqueous phase rearrangement of furfuryl alcohol in one-gallon batch reactor. Reaction conditions: 503 K, 2 min; 500 mL furfuryl alcohol solution and 2000 g water were used for each test.

Initial furfuryl alcohol concentration (wt.%)	Catalyst dosage (g)	Furfuryl alcohol conversion (%)	Carbon yield of 4-hydroxycyclopent-2-enone (%)
20	0.65	100	77.6
40	1.3	100	67.1

In the recent review of Glasnov and Kappe,[21] the continuous flow reactors with a back pressure regulator were suggested to be advantageous for many short time liquid phase reactions. In our future work, the base-promoted aqueous phase rearrangement of furfuryl alcohol and the hydrogenation of hydroxycyclopent-2-enone will be studied with the continuous flow reactors to fulfil the need of industrial continuous production.

As a potential application, a renewable polyurethane was successfully synthesized with diphenyl-methane-diisocyanate and the purified 1,3-cyclopentanediol (98% in purity). The polymerization of diphenyl-methane-diisocyanate and 1,3-cyclopentanediol was carried out at 353 K for 4 h. The method for the purification of 1,3-cyclopentanediol and the detail information for the polymerization test were described in supporting information. According the amount of polyurethane product, 94% carbon yield of polyurethane was obtained. The chemical structure of polyurethane was further confirmed by ^{1}H and ^{13}C NMR spectra and fourier transform infrared spectroscopy (see Figure S9 and Figure S10 of the supporting information). According to the measurement of gel permeation chromatography (see Figure S11 in supporting information), the average molecular weight of the polyurethane as obtained was estimated as 17200. From the results of X-ray powder diffraction, thermogravimetric analysis, melting point analysis and differential scanning calorimetry (see Figure S12, Figure S13 and Table S4 in supporting information), the polyurethane as obtained is amorphous polymer with a melting point of 519-522 K.

Conclusions

In summary, a cyclic monomer for renewable polyurethane, 1,3-cyclopentanediol, was first synthesized at high overall carbon yield (78.3%) by the aqueous phase rearrangement of furfuryl alcohol followed by hydrogenation. The presence of small amount of base catalysts can evidently improve the 4-hydroxycyclopent-2-enone selectivity in the aqueous phase rearrangement of furfuryl alcohol. Under the optimum conditions, a high carbon yield (up to 82.7%) of 4-hydroxycyclopent-2-enone was obtained over the MgAl-HT catalyst with water as the only solvent. Furthermore, it was also noticed that there is a significant solvent effect in the liquid phase hydrogenation of 4-hydroxycyclopent-2-enone to 1,3-cyclopentanediol. When tetrahydrofuran was used as the solvent, high carbon yields of 1,3-cyclopentanediol (>90%)

were obtained over the Ru/C and Raney Ni catalysts. Even in large scale tests with high initial concentration of feedstock, a 72.0% overall carbon yield of 1,3-cyclopentanediol can still be achieved over cheap catalysts (MgAl-HT and Raney Ni), which is favorable for future application. Finally, a polyurethane with an average molecular weight of 17200 was successfully synthesized by the polymerization of diphenyl-methane-diisocyanate and the 1,3-cyclpentanediol as obtained.

Acknowledgements

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