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Highly selective catalytic conversion of furfural to γ-butyrolactone

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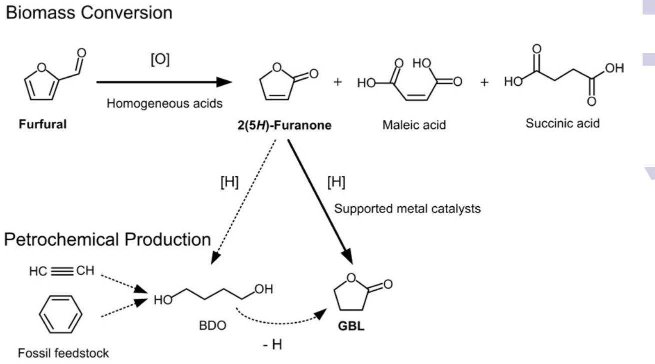
A two-step process was developed for the production of γ-butyrolactone (GBL) from furfural. Furfural was first oxidized using homogeneous acid catalysts under mild conditions in an aqueous/organic bi-phasic system to obtain 2(5*H*)-furanone, which was then selectively hydrogenated to GBL with a high yield over supported metal catalysts.

The conversion of lignocellulosic biomass to fuels and chemicals has received considerable attention due to its environmental, economic, and strategic advantages.[1] Furfural, a renewable platform compound produced by hydrolysis and dehydration of xylan contained in lignocellulose, has already been used to produce fine chemicals such as furfuryl alcohol, tetrahydrofurfuryl alcohol, furan, and furfural resin in industry.[2-4] In recent years, a variety of new processes including oxidation, hydrogenation and hydrogenolysis have been developed for the direct or indirect conversion of furfural into high value-added molecules, such as 1,5-pentanediol, 1,2-pentanediol, cyclopentanone, γ-valerolactone (GVL) and γ-butyrolactone (GBL).[2, 5-9] Among these products, GBL, an important chemical intermediate and solvent that has been widely used in the fields of chemical, medicine, spice and fine organic synthesis, is considered most attractive.[10]

GBL is mainly produced by dehydrocyclization of 1,4-butanediol (BDO) or hydrogenation of maleic anhydride, which is manufactured primarily from fossil feedstock.[11] However, due to the diminishing supply of fossil resource, the current research trend for GBL production moves toward the utilization of renewable resources such as biomass. In earlier studies, furfural was first transformed to tetrahydrofuran (THF) by decarbonxylation and hydrogenation, and THF was then oxidized to produce GBL.[2] However, this method has limitations because of its harsh conditions, complicated process and low yield. Recently, substantial interest has been devoted to the selective oxidation of furfural to acid anhydrides or dicarboxylic acids, which can be used for the synthesis of diols and lactones. Lan *et al.*[12] reported the aerobic oxidation of furfural to 54.0% yield of maleic anhydride with $H_5PV_2Mo_{10}O_{40}$ and $Cu(CF_3SO_3)_2$ as catalysts, while Choudhary *et al.*[13] realized aqueous oxidation of furfural to succinic acid (SA) in 74.2% yield using Amberlyst-15 as catalyst. Maleic anhydride or SA can then be used to produce GBL, BDO and THF, whereas noble metal catalysts with a high loading, high pressure (5~20 MPa) and high temperature (423~573 K) are generally needed.[14]



Scheme 1 Illustration of the proposed conversion of furfural to GBL.

In addition to dicarboxylic acids and acid anhydrides, furfural can also be oxidized to 2(5*H*)-furanone. The molecule structure of 2(5*H*)-furanone contains only one additional C=C bond than GBL, making it a potential intermediate for the conversion of furfural to GBL. Cao *et al.*[15] reported a convenient synthesis of 2(5*H*)-furanone from furfural by autocatalysis with dichloroethane as solvent, but more than 10 hours were required to obtain a 37% yield. Badovskaya *et al.*[16] investigated furfural oxidation in the presence of Mo (VI) or Cr (VI), but did not get an improved yield of 2(5*H*)-furanone. Although the oxidation of furfural to 2(5*H*)-furanone has been studied for decades, most works use homogeneous catalysts and chlorinated solvents and the yield of 2(5*H*)-furanone is still moderate ranging from 30~50%. The atom economy of producing GBL from furfural with 2(5*H*)-furanone as intermediate is much higher than that with dicarboxylic acid or anhydride as intermediate, but few studies have been reported on the hydrogenation of 2(5*H*)-furanone.

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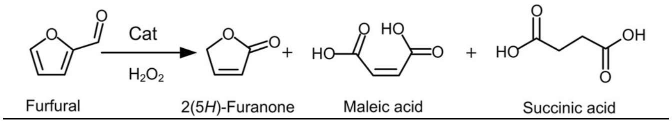
Herein, we report a two-step process to produce GBL from the biomass derived platform compound furfural with 2(5*H*)-furanone as the intermediate (Scheme 1). In the first step, furfural was oxidized to 2(5*H*)-furanone with a yield of 61.5% in a bi-phasic system using formic acid as catalyst, ethyl acetate as solvent and hydrogen peroxide as oxidant. In the second step, the purified 2(5*H*)-furanone was further hydrogenated to GBL using supported metal catalysts. Pd0.5/SiO_2 gave the best performance among the selected catalysts, with a high GBL selectivity of 92.6% when 2(5*H*)-furanone was completely converted. To the best of our knowledge, this is the first report on selective hydrogenation of 2(5*H*)-furanone to GBL.

In the initial studies of furfural oxidation, various homogeneous and heterogeneous acid catalysts were evaluated using 1,2-dichloroethane as solvent (Table S1). The blank experiment without catalyst gave a 2.6% yield of 2(5*H*)-furanone at a very low conversion. Among the selected acid catalysts, formic acid was found to exhibit the highest activity for converting furfural to 2(5*H*)-furanone, with a 60.3% yield of 2(5*H*)-furanone obtained. The reason for this high yield is that formic acid can react with hydrogen peroxide to generate performic acid, which is the real active oxidant with strong oxidizing nature and good solubility in both aqueous and organic phases. The molar ratio of formic acid/furfural was optimized (Figure S1). When other acid catalysts were used, SA or maleic acid (MA) was the main product and the yield of 2(5*H*)-furanone was less than 20%.

The solvent plays an important role in oxidation of furfural to 2(5*H*)-furanone. To study the solvent effect, the furfural oxidation reaction was carried out in both bi-phasic and homogeneous systems using a variety of solvents with formic acid as catalyst and hydrogen peroxide as oxidant. When 1,2-dichloroethane, tetrachloromethane, benzene, toluene, ethyl acetate or distilled water was used as solvent (Table 1, entries 1-6), a bi-phasic reaction system consisting of an aqueous phase and an organic phase was formed. A 60.3% yield of 2(5*H*)-furanone was obtained from the organic phase when using 1,2-dichloroethane as solvent, meanwhile the water soluble byproducts MA and SA were in the aqueous phase with a yield of 12.0% and 6.3%, respectively. When tetrachloromethane was used as solvent, the yield of 2(5*H*)-furanone decreased to 40.2%. However, the introduction of benzene or toluene as solvent caused severe non-catalytic polymerization of furfural, and the liquid turned brown gradually. Considering the environmental issues, water or organic solvents with low toxicity are preferred.[17] When distilled water was used as solvent, the yield of 2(5*H*)-furanone was only 3.2% (Table 1, entry 6). By decreasing the amount of furfural for complete dissolution in water, the yield of 2(5*H*)-furanone was increased to 27.8% (Table 1, entry 7). Ethyl acetate, a moderate solvent with low toxicity, was found to be an ideal substitute for 1,2-dichloroethane, giving 61.5% yield of 2(5*H*)-furanone, 6.7% yield of MA and 8.5% yield of SA. In homogeneous systems with methanol, isopropanol, GBL and THF as solvents (Table 1, entries 8-11), SA was the major product and the yields of 2(5*H*)-furanone and MA were below 20%. Besides, the yield of SA was improved with an increase in the dielectric constant of the solvent. The formation of some GC and HPLC-silent products via polymerization or deep oxidation caused incomplete carbon balance. In the bi-phasic system, 2(5*H*)-furanone and the water soluble byproducts like MA and SA were separated simply by stratification after the reaction. 2(5*H*)-furanone was separated from the organic phase through vacuum distillation. The purification of 2(5*H*)-furanone prevented the introduction of acid compounds such as formic acid into the hydrogenation reaction system, which may accelerate side reactions and decrease the selectivity to GBL. The purified 2(5*H*)-furanone was then hydrogenated in the second step.

Having obtained 2(5*H*)-furanone by furfural oxidation, we next turn to the hydrogenation of 2(5*H*)-furanone to GBL. 2(5*H*)-furanone has two unsaturated bonds, namely the conjugated C=O

Table 1 Reaction results of furfural oxidation with different solvents [a]



Entry	Solvent	Yield [b] (%)			
		2(5*H*)-furanone	MA	SA	Total
1	1,2-dichloroethane	60.3	12.0	6.3	78.6
2	Tetrachloromethane	40.2	11.3	8.6	60.1
3	Benzene	8.9	7.3	10.1	26.3
4	Toluene	12.2	9.2	4.9	26.3
5	Ethyl acetate	61.5	6.7	8.5	76.7
6	Distilled water	3.2	1.1	4.7	9.0
7 [c]	Distilled water	27.8	8.1	39.8	75.7
8	Isopropanol	11.3	11.3	26.4	49.0
9	Methanol	13.1	12.0	35.3	60.4
10	GBL	12.8	17.3	38.3	68.4
11	THF	18.2	10.0	25.6	53.8

[a] Reaction conditions: furfural (4.0 g), solvent (10 mL), H_2O_2 (30%, 10 mL), Na_2SO_4 (4.0 g), formic acid (88%, 1.5 mL), 333 K, 3 h. [b] The yields of products were calculated when furfural was just completely converted. [c] Furfural was completely dissolved in the solvent (1 g furfural/ 9 mL distilled water) and the reaction system turned to be homogeneous, in nitrogen .

Table 2 Properties and catalytic performances of SiO_2 supported Group VIII metals

Entry	Catalyst [a]	CO-uptake [b] (10^{-6} mol/g)	Metal dispersion (%)	k_r [d, f] (10^{-2}min^{-1})	Selectivity to GBL [e,f] (%)
1	Ni4.5/SiO_2	18.9	2.5	2.4	91.6
2	Co4.5/SiO_2	22.5	2.9	1.8	87.2
3 [c]	Cu4.5/SiO_2	—	1.8	0.3	91.4
4	Pt0.5/SiO_2	3.7	14.5	1.4	70.4
5	Pd0.5/SiO_2	2.2	4.7	7.8	92.6
6	Rh0.5/SiO_2	3.0	6.1	7.7	91.3
7	Ru0.5/SiO_2	2.1	4.3	1.6	89.2

[a] The monometallic catalysts were denoted as M*x*/SiO_2, where *x* was the loading in wt% of the supported metals. [b] Each absorbed CO molecule was assumed to correspond to one active site. [c] The metal dispersion of Cu was determined by H_2-N_2O titration. [d] The reaction order was fixed at 1.0. [e] The selectivity to GBL was calculated with 2(5*H*)-furanone just completely converted. [f] Reaction conditions: 2(5*H*)-furanone (6.0 g), catalyst (0.6 g), methanol as solvent (100 mL), 353 K, 3. MPa H_2, 180 mL/min H_2 gas flow, 800 r/min stirring.

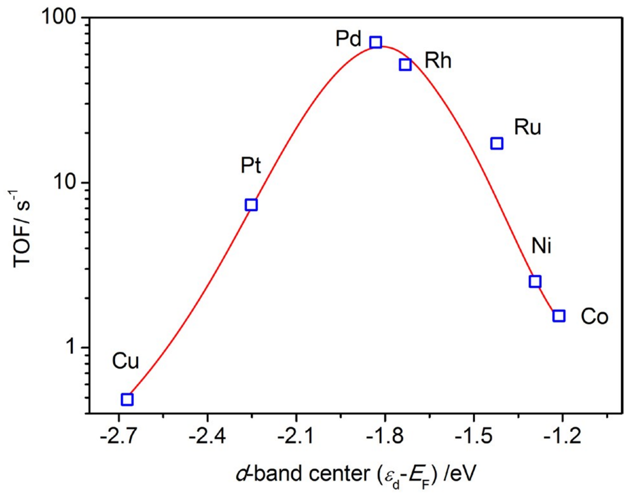


Fig 1 Correlation of initial TOF for 2(5*H*)-furanone hydrogenation with *d*-band center relative to Fermi level. 2(5*H*)-furanone (6.0 g), catalyst (0.6 g), methanol as solvent (100 mL), 353 K, 3.5 MPa, 180 mL/min H_2 gas flow, 800 r/min stirring.

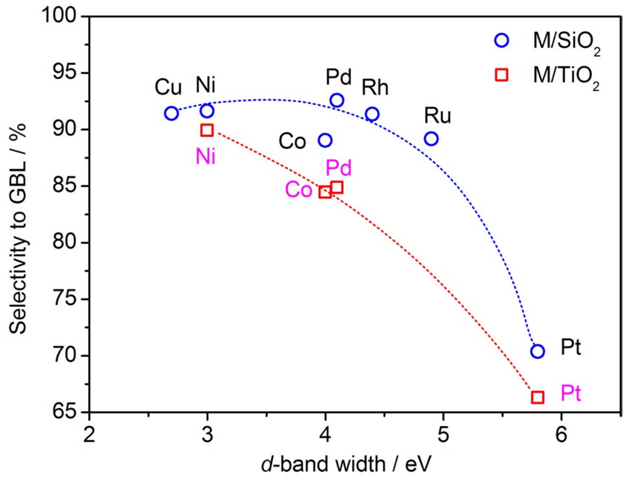


Fig 2 Correlation of the selectivity to GBL with *d*-band width. 2(5*H*)-furanone (6. g), catalyst (0.6 g), methanol as solvent (100 mL), 353 K, 3.5 MPa, 180 mL/min H gas flow, 800 r/min stirring.

and C=C bonds. The selective hydrogenation of C=C bond over SiO_2 or TiO_2 supported Group VIII metals was studied in liquid phase. A series of SiO_2 and TiO_2 supported metal (M = Pt, Pd, Rh, Ru, Ni, Co and Cu) catalysts were prepared by incipient wetness impregnation. TEM and Chemisorption were respectively used to estimate the metal particle size distribution (Figure S2) and the metal dispersion (Table 2, Table S2) of the catalysts. As listed in Table 2, significant differences exist in the reaction rate and product distribution among different metal catalysts. The Pd0.5/SiO_2 catalyst showed a better performance than the others, giving a reaction rate constant of 0.078 min^{-1} and GBL selectivity of 92.6%. Moreover, the Pd0.5/SiO_2 catalyst was found to be stable and reusable, retaining its hydrogenation activity and selectivity to GBL after 5 runs (Figure S3). The Ni4.5/SiO_2 catalyst had the highest activity (0.024 min^{-1}) and selectivity to GBL (91.6%) among the selected non-noble metal catalysts. From the view of cost, Ni4.5/SiO_2 is much cheaper than Pd0.5/SiO_2 for industrial applications. For the SiO_2 supported metal catalysts, the reaction rate constant followed the trend of Pd0.5/SiO_2 ~ Rh0.5/SiO_2 > Ru0.5/SiO_2 > Pt0.5/SiO_2, and Ni4.5/SiO_2 > Co4.5/SiO_2 > Cu4.5/SiO_2. When Ni, Co, Pt and Pd were supported on TiO_2, the reaction rate constants were 0.025 min^{-1}, 0.018min^{-1}, 0.015min^{-1} and 0.047 min^{-1}, respectively, showing a similar trend to that of the SiO_2 supported catalysts. The decrease of hydrogenation activity of the Pd0.5/TiO_2 catalyst with a lower reaction rate constant than that over Pd0.5/SiO_2 may be caused by the partial coverage of metal active sites due to the strong metal-support interaction.

To further discuss the catalyst activity, the initial turnover frequency (TOF) for 2(5*H*)-furanone hydrogenation over the SiO_2 supported metal catalysts is plotted in Figure 1 as a function of the *d*-band center (ε_d) relative to the Fermi level (E_F). The number of active sites was determined by chemisorption, and the values of ε_d were taken from *ref* 18. A volcano-type relationship was observed with Pd showing the maximum activity. A similar volcano-type correlation was obtained when using the number of active sites estimated from the TEM images (Figure S4). The *d*-band center is a useful parameter to describe electronic state of the entire valence band of the metal surface, which is responsible for the activities of metal catalysts.[19] The volcano-type relationship between activities and *d*-band center has been established for several other reaction systems.[20] According to the *d*-band model proposed by Nørskov, the binding energy of adsorbates decreases when the *d*-band center shifts away from the Fermi level.[21] The binding energies of small absorbates such as hydrogen, alkene containing C=C bond and oxygenates containing C=O bond have been correlated with the *d*-band center for Group VIII metals.[22] The nearly linear correlations verify the effectiveness of Nørskov's model. Therefore, the binding energy of 2(5*H*)-furanone over the selected Group VIII metals is considered to follow the trend of Cu < Pt < Pd < Rh < Ru < Ni < Co. The curve in Fig 1 indicates that the value of the *d*-band center of Pd corresponds to a 2(5*H*)-furanone binding energy that is optimal for hydrogenation. Stronger binding energy may lead to surface poisoning, while weaker binding energy may limit the availability of 2(5*H*)-furanone, therefore in both cases the catalytic activities are lower than the optimal.

As shown in Table 2, a wide variation in selectivity to GBL is observed over different SiO_2 supported metal catalysts. Among the selected metals, Ni, Pd and Rh are more selective towards C=C hydrogenation than C=O hydrogenation and the ring opening, with a selectivity of 91.6%, 92.6% and 91.3%, respectively. Figure 2 shows a plot of selectivity to GBL vs the width of the metal *d*-band, which is an empirical indicator of the electronic structure of the transition metals.[19, 23] It can be seen that the narrower the width of the metal *d* band, the higher the selectivity to GBL. This is consistent with the theoretical calculations reported by Delbecq and Sautet[23], who showed that a narrower *d*-band width allowed greater interaction between the C=C bond and metal surface and benefited the selective hydrogenation of C=C bond. However, when the *d*-band width decreased to a certain value, a slight decrease of selectivity was observed. When Ni, Co, Pt and Pd were supported on TiO_2, a similar trend in selectivity to GBL was obtained. For the same metal, the selectivity to GBL over M/TiO_2 was lower than that over M/SiO_2. This may be due to the partial coverage of the metal active sites and the generation of new sites that can accelerate side reactions (Figure S5). The decreased selectivity to GBL is mainly caused by polymerization of cyclic organics and side reactions including hydrogenation of C=O bond, ring opening and excess hydrogenation.

Conclusions

A two-step process for production of GBL from furfural was developed, providing a new strategy for converting biomass derived platform compound to high value-added fine chemicals. The highest yield of 2(5*H*)-furanone (61.5%) was obtained from furfural oxidation reaction in a bi-phasic system with formic acid as catalyst, ethyl acetate as solvent, and hydrogen peroxide as oxidant. Then 2(5*H*)-furanone was further hydrogenated to GBL with a high selectivity of 92.6% over Pd0.5/SiO_2 when 2(5*H*)-furanone was completely converted. The initial TOF for 2(5*H*)-furanone hydrogenation over SiO_2 supported Group VIII metals (M= Pt, Pd, Rh, Ru, Ni, Co and Cu) showed a volcano-type dependence on the ε_d-E_F value, with Pd having the highest activity. The variation of selectivity to GBL over different supported metal catalysts was rationalized on the basis of the *d*-band width. These correlations can guide the design of more efficient catalysts for the hydrogenation of 2(5*H*)-furanone to GBL.

Acknowledgments

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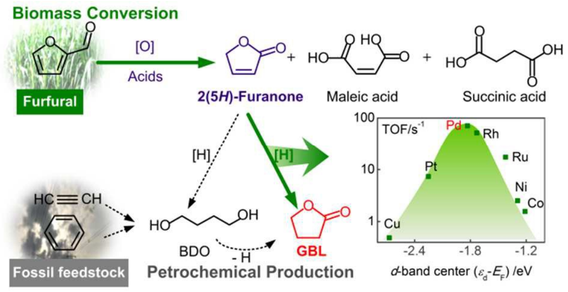

A two-step strategy consisting of furfural oxidation and selective hydrogenation of 2(5*H*)-furanone was developed to produce γ-butyrolactone from furfural.