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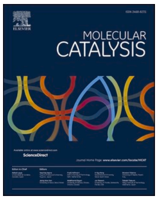

Feasible synthesis of bifurfural from renewable furfural derived 5-bromofurfural for polymerization

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ABSTRACT

Deriving versatile monomers from bulky biomass for polymer production can greatly replace fossil resources as the carbon source of chemical industry. The present studies introduce the feasible synthesis of bifurfural, a bifunctionalized bifuran monomer, from the furfural platform. The reaction was carried out through reductive coupling of 5-bromofurfural with CO as the reductant source with commercial Pd/C as the catalyst under gentle conditions, and the catalyst is recyclable and reusable. So prepared bifurfural was preliminarily investigated as a monomer for poly(Schiff base) material synthesis, and it was found that the poly(Schiff base) derived from nonlinear bifurfural monomer polymerizing with linear *p*-phenylenediamine demonstrated larger surface area than that from petrochemical 4,4′-biphenyldicarboxaldehyde with excellent thermal stability, thus offering a new opportunity in bifurfural based furfural utilization in polymer industry.

1. Introduction

With the rapid depletion of fossil resources, the search for their replacements as the carbon sources of chemical industry has attracted much attention for a long while. For this purpose, biomass is the most attractive candidate, because of its annual availability and mostly non-competitive with the food supply of human beings. [1] In order to achieve the replacement of fossil resources with sustainable biomass, the exploration of the new catalytic technologies to derive versatile bio-based monomers for polymer synthesis is extremely crucial, because the polymer production consumes the most dominant carbon sources in chemical industry. Therefore, deriving novel monomers from sustainable biomass with related studies on their polymerization has become the hot topics in academic and industrial communities, and the successful examples include the synthesis of γ-methyl-α-methylene-γ-butyrolactone and 2,5-furandicarboxylic acid. [2-4] Remarkably, both of them are produced from hydroxylmethylfurfural (HMF), a C6 based platform compound, in which γ-methyl-α-methylene-γ-butyrolactone is synthesized from levulinic acid that is a rehydration product of HMF, and 2,5-furandicarboxylic acid is an oxidation product of HMF. [5-10] Although HMF can be ideally produced from raw cellulose through acid-catalyzed hydrolysis followed by dehydration, because of its instability under the acidic hydrolysis conditions, [11,12] HMF is currently produced from dehydration of glucose and fructose, which is competitive with the food supply of human beings. [13]

In the contrast, furfural is ongoing industrially produced from raw hemicellulose in agricultural byproducts; [14] the challenge is that, unlike HMF, furfural has a monofunctionalized furan structure, thus its utilization in polymer synthesis is seriously limited, making its current market volume still <0.5 Mt/y, much less than its potential production capability. In view of its easy availability from bulk raw hemicellulose, the exploration of new catalytic technologies to transform the furfural platform into versatile bifunctionalized monomers attracted much attention in recent years, [15] including its hydrogenation to diol, [16-18] oxidation to maleic anhydride, [19-22] oxidation ring-opening to aliphatic diacid, [23-31] Friedel-Crafts alkylation to the analogues of bisphenol A, [32,33] and so on. Since 2011, our laboratory was involved in catalytic aerobic oxidation of furfural to maleic acid and anhydride, [22,24,25] and most recently was involved in catalytic transformation of its sub-products into bifunctionalized furan and bifuran monomers, including bromination-carbonylation of furoic acid to 2,5-furandicarboxylic acid, [34-37] carbonylation of 5-bromofurfural to 5-formyl-2-furancarboxylic acid, [38] oxidative coupling of furfuryl acetate to HMF derivatives, [39] and reductive coupling of 5-bromofuroic acid to 2,2-bifuryl-5,5-dicarboxylic acid. [40] Remarkably, the prepared

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polyesters from the condensation of 2,2-bifuryl-5,5-dicarboxylic acid with aliphatic diols displayed the lower liquid crystalline phase transition temperature than those from its petrochemical based analogue, 4, 4'-biphenyldicarboxylic acid, thus demonstrating more flexible machinability.

As well as 2,2-bifuryl-5,5-dicarboxylic acid alternative to 4,4'-biphenyldicarboxylic acid, bifurfural is a furan based surrogate of 4,4'-biphenyldicarboxaldehyde. In the literature, Taljaard and Kasuya independently reported its synthesis through oxidative coupling of furfural with $Pd(OAc)_2$ catalyst in HOAc under 50 atm of O_2 or in HOAc/DMSO with O_2 balloon. [41,42] Further studies by Kasuya on its poly (Schiff-base) synthesis with aliphatic diamines disclosed that bifurfural based poly(Schiff base) could be the promising biobased materials, as they could be molded into films with good strengths, and were tough to bend. [42] Since covalent organic frameworks synthesized through the condensation of nonlinear monomers may have higher specific surface area and micropore volume than that of linear ones, [43] as a nonlinear dialdehyde, condensation of bifurfural with diamines may provide so-prepared poly(Schiff base) materials to demonstrate some properties different from those from linear 4,4'-biphenyldicarboxaldehyde. Here, we introduce a new catalytic route for bifurfural synthesis through reductive coupling of 5-bromofurfural by using commercial Pd/C as the catalyst with CO as the reductant source. Remarkably, in the preliminary polymer synthesis studies, using the synthesized bifurfural to polymerize with linear *p*-phenylenediamine disclosed that so prepared poly (Schiff base) has a higher surface area than those from petrochemical derived 4,4'-biphenyldialdehyde with satisfactory thermal stability, whereas its polymerization with *m*-phenylenediamine demonstrated a smaller surface area than that from 4,4′-biphenyldicarboxaldehyde, thus providing an alternative opportunity for synthesis of poly(Schiff base) materials with different properties. Because of the limited usage as an intermediate in pharmaceutical synthesis, [46,47] 5-bromofurfural is currently produced in a very limited volume through furfural bromination, [44,45] however, in the case of that bifurfural can be employed as a monomer for practical polymer synthesis, it may substantially expand 5-bromofurfural base furfural utilization, and make the improvement on the production efficiency of 5-bromofurfural from furfural on a large scale becoming very important.

2. Experimental

2.1. Materials and instruments

5-Bromofurfural and Pd/C (wetted with ca. 55% water) were purchased from Shanghai Bi De Pharmaceutical Technology Co., Ltd. Ru/C was from Shanghai Maclean Biochemical Technology Co., Ltd. Pt/C and Pd/SiO_2 were from Saan Chemical Technology (Shanghai) Co., Ltd. Pd/Al_2O_3 and *m*-phenylenediamine were from Aladdin Reagent (Shanghai) Co., Ltd. $Pd/CaCO_3$, $Pd/BaSO_4$ and *p*-Phenylenediamine were from Shanghai Meryer Biochemical Technology Co., Ltd. 4,4'-Biphenyldicarboxaldehyde was from Shanghai XianDing Biological Science & Technology Co., Ltd. All of the bases were purchased from Sinopharm Chemical Reagent Co., Ltd.

^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400 using TMS as an internal reference. The images of catalysts were observed by a scanning electron microscopy (Nova Nano SEM, America). X-ray Photoelectron Spectroscopy (XPS) was obtained in a VG multilab 2000 spectrometer using a Mg-Al Ka X-ray source with the passing energy flow of 100 eV. Fourier transform infrared (FT-IR) spectra were collected on a Bruker Tensor 27 FT-IR spectrometer in KBr medium. The content of palladium in the reaction solution was determined by inductively coupled plasma spectrometer (ICAP 7200 Plus), and the palladium leaching from the Pd/C catalyst was calculated from the ICP analysis. Thermal stability measurements were conducted using a thermogravimetric analysis (TGA) instrument (PerkinElmer TGA 8000, America), in which the samples were heated at a heating rate of 10°C /min from 30 to 800°C in a N_2 flow of 30 mL/min. The N_2 physical adsorption-desorption measurement was carried out on an Autosorb-1 Quantachrome instrument. The specific surface areas of prepared poly(Schiff base) were calculated using the Brunauer-Emmet-Teller (BET) model, and the pore size distributions was calculated from the adsorption isotherms by nonlocal density functional theory (NLDFT) assuming a slit pore geometry with equilibrium model. The powder X-ray diffraction (PXRD) patterns were obtained by using Rigaku D/Max 3400 powder diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm).

2.2. Analytical methods

The product was typically analyzed by HPLC. After a typical catalytic reaction, the product mixture was diluted with a mobile phase of known mass, then filtered and analyzed by HPLC. The HPLC instrument was equipped with a UV detector and a C18 column (250 mm × 4.6 mm); the mobile phase was CH_3CN/H_2O (45%: 55%, v/v) and the flow rate was 1 mL/min. The column temperature was 30°C and the wavelength of UV detector for bifurfural and 5-bromofurfural analysis was set at 260 nm.

2.3. Synthesis of bifurfural through reductive coupling of 5-bromofurfural with CO balloon

5-Bromofurfural (35.0 mg, 0.2 mmol), Pd/C (47 mg, 20 μmol) and $KHCO_3$ (50.0 mg, 0.5 mmol) were successively added in CH_3CN (2 mL) in a glass tube. The reaction tube was evacuated and backfilled with CO (three times, balloon) and then heated to 75°C with a CO balloon under stirring for 6 h. After the reaction, the reaction mixture was cooled down to room temperature and carefully vented to drain excess CO in a fume hood. The yield of bifurfural and the conversion of 5-bromofurfural were quantitatively analyzed by HPLC.

2.4. The reusing test of the Pd/C catalyst for reductive coupling of 5-bromofurfural to bifurfural

In reusing tests of catalyst for this reaction, to resolve the problem from the catalyst loss in its recycling process, at the first run, five sets of the identical experiments were conducted in parallel, and four identical ones were next paralleling conducted at the second run, and so on. Through this procedure, the loss of the catalyst during the recycling process can be compensated from one more experiment in an earlier run, and the last reusing test was the 5th cycle. The detailed experiments were described as follows.

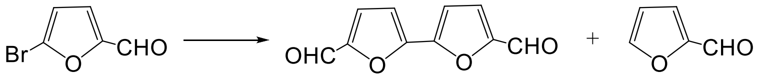
5-Bromofurfural (35.0 mg, 0.2 mmol), Pd/C (47 mg, 20 μmol) and $KHCO_3$ (50.0 mg, 0.5 mmol) were successively added in CH_3CN (2 mL) in a glass tube. The reaction tube was evacuated and backfilled with CO (three times, balloon) and then heated to 75°C with a CO balloon under stirring for 6 h. The identical reaction was conducted paralleling in five sets. After the reaction, these reaction mixtures were combined together, heated and filtered to get the Pd/C catalyst precipitates. The resulting Pd/C catalyst was washed with water and ethanol, and then dried overnight in a vacuum at 30 °C, which was employed as the catalyst for the second cycle. On the other side, the resulting supernatants after catalyst filtration were vapored under reduced pressure to remove the solvent, and a yellow product was precipitated, which was next washed with water to remove salt to give the bifurfural product. The recovered Pd/C catalyst from the first cycle was charged as the catalyst for the second cycle, and the identical reaction was conducted paralleling in four sets, and so on. The last reusing test was the 5th cycle experiment, which still provided 89% yield of bifurfural with 90% conversion in HPLC analysis.

2.5. Gram level synthesis of bifurfural

5-Bromofurfural (1 g, 5.7 mmol), Pd/C (1.34 g, 10 mol%) and $KHCO_3$ (1.18 g, 14 mmol) were successively added in CH_3CN (50 mL) in

Table 1

Catalyst scanning for the reductive coupling of 5-bromofurfural to bifurfural[a].



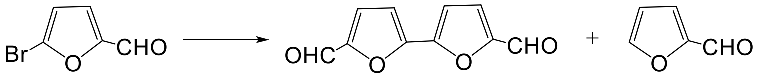
5-bromofurfural bifurfural furfural

Entry	Catalyst	Conv.(%)	Yield(%)	
			bifurfural	furfural
1	Pd/C	>99	98	<1
2	Pt/C	<1	<1	<1
3	Ru/C	7	<1	<1
4	Pd/Al_2O_3	65	35	6
5	$Pd/BaSO_4$	17	13	1
6	$Pd/CaCO_3$	12	7	3
7	Pd/SiO_2	9	7	<1

[a] Conditions: 5-bromofurfural (0.2 mmol), catalyst (20 μmol), $KHCO_3$ (0.5 mmol), CH_3CN (2 mL), 75°C, CO balloon, 6 h.

Table 2

The influence of the reductant sources on the reductive coupling of 5-bromofurfural to bifurfural[a].



5-bromofurfural bifurfural furfural

Entry	Reductant	Conv.(%)	Yield (%)	
			bifurfural	furfural
1	CO	>99	98	<1
2[b]	methanol	71	37	3
3	ethanol	63	33	3
4	isopropanol	30	5	2
5[c]	dimethylformamide	52	13	2

[a] Conditions: 5-bromofurfural (0.2 mmol), Pd/C (20 μmol), $KHCO_3$ (0.5 mmol), CH_3CN (2 mL), 75°C, reductant, 6 h. [b]60°C. [c]100°C.

a round-bottomed flask. The flask was evacuated and backfilled with CO (three times, balloon) and then heated to 75°C with a CO balloon under stirring for 20 h. After the reaction, the Pd/C catalyst was removed through hot filtration, and the catalyst was washed with hot CH_3CN for five times to completely dissolve the absorbed bifurfural product from the Pd/C catalyst. Next, the combined supernatants were vapored under reduced pressure to obtain the yellow precipitate which was next washed with water and dried to give the bifurfural product, yield: 90% (0.49 g).

2.6. Synthesis of poly(Schiff base) materials from bifurfural with phenylenediamine

Using prepared bifurfural as one monomer, poly(Schiff base) material was synthesized through its polymerization with phenylenediamine by the modified procedures from the literatures, [43,48,49] and similar syntheses were conducted by using 4,4'-biphenyldicarboxaldehyde instead of bifurfural for comparison. In a typical procedure, bifurfural (0.5 mmol) and *p*-phenylenediamine (0.5 mmol) in DMSO (5 mL) were added in a 15 mL flask. After stirring at 50°C for 20 min under N_2 atmosphere, the reaction mixture was heated up to 180°C for 10 h. After cooling down to room temperature, the obtained crude product was filtered and washed with dimethylformamide, acetone and dichloromethane several times, respectively, and dried in a vacuum oven to obtain the red poly(Schiff base) product, yield: 75% (119.4 mg).

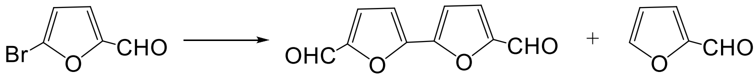
3. Results and discussion

Since 5-bromofurfural is not water soluble, catalytic synthesis of bifurfural from 5-bromofurfural through reductive coupling was conducted in CH_3CN with CO balloon as the reductant source, and the scanning of different supported catalysts was investigated initially. As shown in Table 1, in the presence of $KHCO_3$ as the base, using commercial Pd/C as the catalyst achieved almost complete conversion of 5-bromofurfural with 98% yield of bifurfural formation, and less than 1% furfural was observed as a dehalogenation product in 6 h (Table 1, entry 1). Neither Pt/C nor Ru/C was active for this reductive coupling reaction, giving <1% or 7% of conversion with less than <1% yield of bifurfural formation under the identical conditions of the Pd/C catalyst (Table 1, entries 2 and 3). It is worth mentioning that, in organic synthesis, similar better activity of palladium than other metal catalysts was also popularly observed in other C-C coupling reaction through C-Br activation. [50-52] Next, other supported Pd catalysts were also tested as well. As shown, using Pd/Al_2O_3 as the catalyst provided 65% conversion with 35% yield of bifurfural and 6% yield of furfural, and $Pd/BaSO_4$ provided 17% conversion with 13% yield of bifurfural (Table 1, entries 4 and 5). $Pd/CaCO_3$ and Pd/SiO_2 were very poor for this catalysis, giving only 12% and 9% of conversion (Table 1, entries 6 and 7), respectively. The better activity of activated carbon as the support for this reaction may be attributed to its higher surface area than others, which facilities the high dispersion of palladium with efficient absorption of 5-bromofurfural substrate on the support for catalysis. Taken together, commercial Pd/C catalyst was the best candidate for this reductive coupling reaction; thereof, in view of its feasible availability, coming investigations were focused on using Pd/C as the catalyst. Investigation of the reaction temperature disclosed that increasing the temperature continuously accelerated the reaction, leading to improved conversion and bifurfural yield, and at 75°C, it reached >99% conversion with 98% yield of bifurfural (Table S1). Similarly, increasing the dose of the catalyst also accelerated the conversion of substrate, and at the dose of 20 and 25 μmol catalyst, it provided >99% conversion with 98% and 99% yield of bifurfural, respectively (Table S2). In view of that the Pd/C catalyst is reusable, 20 μmol of the Pd/C catalyst were employed in coming studies.

Next, different reductant sources were investigated for this reaction and the results are summarized in Table 2. As shown, using methanol as

Table 3

The influence of base on the reductive coupling of 5-bromofurfural to bifurfural[a].



5-bromofurfural bifurfural furfural

Entry	Base	pKa	Conv. (%)	Yield (%)	
				bifurfural	furfural
1	-	-	15	12	<1
2	$NaHCO_3$	8.1	73	69	<1
3	$KHCO_3$	8.4	>99	98	<1
4	Na_2CO_3	11.5	86	77	<1
5	K_2CO_3	11.6	>99	72	<1
6	Cs_2CO_3	11.6	>99	68	<1
7	KOH	13.2	>99	13	<1
8	NaOH	13.2	>99	<1	<1

[a] Conditions: 5-bromofurfural (0.2 mmol), Pd/C (20 μmol), base (0.5 mmol), CH_3CN (2 mL), 75°C, CO balloon, 6 h.

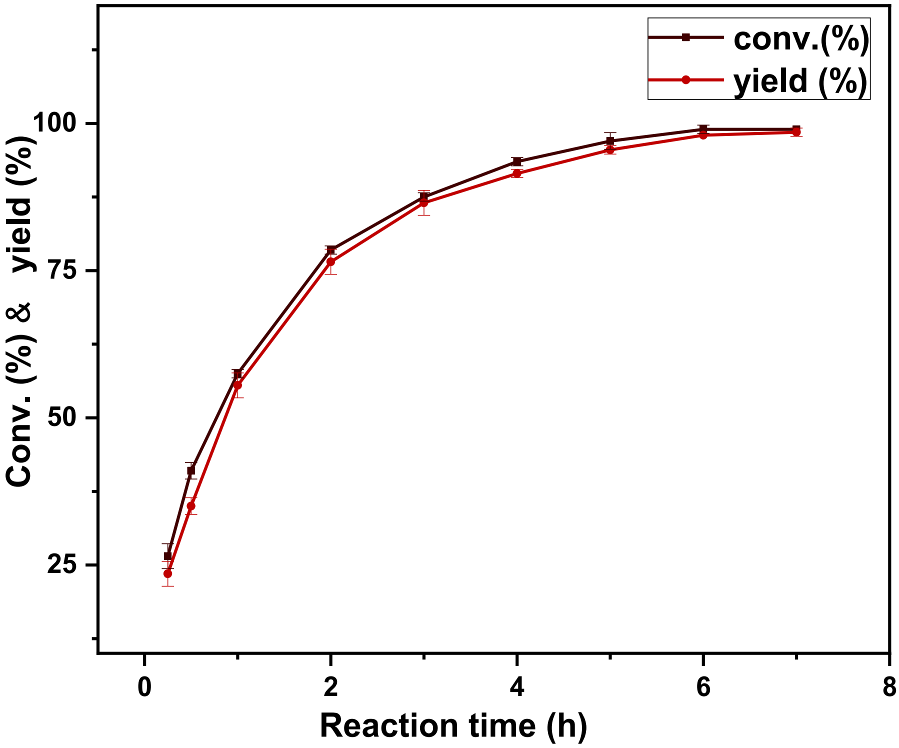


Fig. 1. The time-course of reductive coupling of 5-bromofurfural to bifurfural. Conditions: 5-bromofurfural (0.2 mmol), Pd/C (20 μmol), $KHCO_3$ (0.5 mmol), CH_3CN (2 mL), 75 °C, CO balloon.

the reductant provided 71% conversion with 37% yield of bifurfural and 3% yield of furfural (Table 2, entry 2), in which the reaction was conducted at 60 °C due to the low boiling point of methanol. Ethanol as the reductant offered 63% conversion with 33% yield of bifurfural and 3% yield of furfural, and isopropanol gave 30% conversion with 5% yield of bifurfural and 2% yield of furfural (Table 2, entries 3 and 4). Clearly, alcohol as the reductant was less efficient than CO for this reductive coupling reaction, and little more furfural was generated as a dehalogenation product due to their hydrogen supplement ability. As evidence, when using hydrogen as the reducing agent, it fully converted 5-bromofurfual to furfural without bifurfural formation. In addition, dimethylformamide was also tested as the reductant at 100 °C, which provided 52% conversion with 13% yield of bifurfural and 2% yield of furfural (Table 2, entry 5). Taken together, CO is the best reductant for the reductive coupling of 5-bromofurfural to bifurfural as well as it in the reductive coupling of 5-bromofuroic acid to 2,2-bifuryl-5,5-dicarboxylic acid. [40] Remarkably, CO is also a sustainable resource because it can be obtained through biomass refinery, [53] thus making this process fully sustainable in view of its carbon sources.

In dehalogenation reactions, the presence of base is essential for efficient catalysis because of its capability in halogen removal from the catalytic site. [34-38,40,54] Here, the influence of different bases was investigated for this reductive coupling reaction in CH_3CN with CO as the reductant source (Table 3). As shown, in the absence of base added, it provided only 15% conversion with 12% yield of bifurfural (Table 3, entry 1). Adding $NaHCO_3$ having a pKa value of 8.1 gave 73% conversion with 69% yield of bifurfural and less than 1% yield of furfural as a dehalogenation product (Table 3, entry 2). A just slightly stronger base, $KHCO_3$ having a pKa value of 8.4 achieved >99% conversion with 98% yield of bifurfural (Table 3, entry 3). Remarkably, the time-course of this reductive coupling reaction by using $KHCO_3$ as the base disclosed that it was a highly selective process for bifurfural formation as displayed in Fig. 1. However, the stronger bases including Na_2CO_3, K_2CO_3 and Cs_2CO_3 having pKa values of 11.5, 11.6 and 11.6, respectively, made the

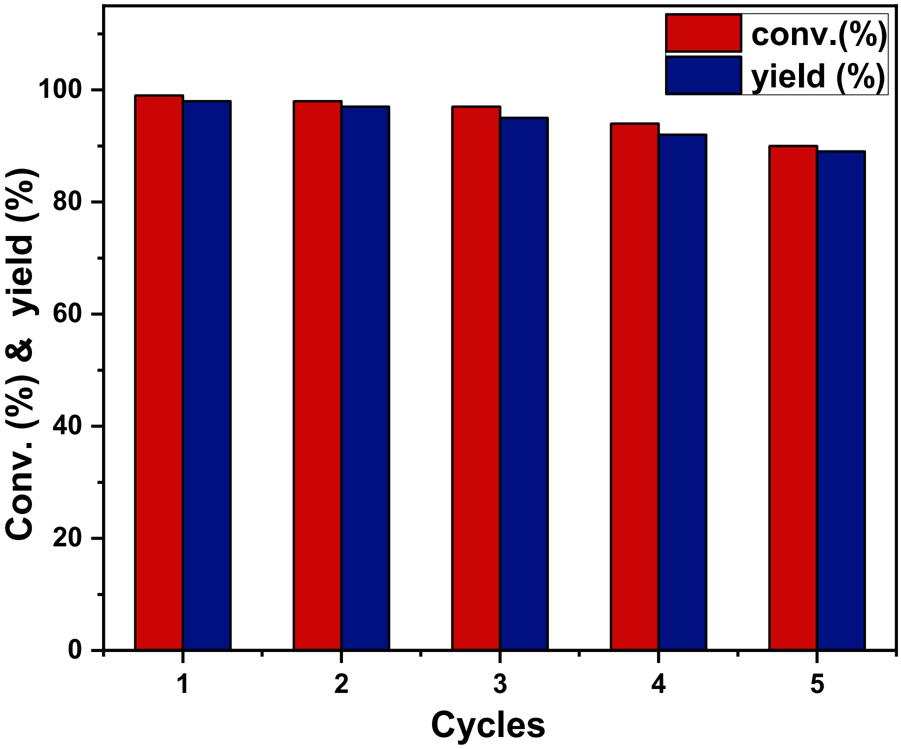


Fig. 2. The reusing test of the Pd/C catalyst for the reductive coupling of 5-bromofurfural to bifurfural. Conditions: 5-bromofurfural (0.2 mmol), Pd/C (20 μmol), $KHCO_3$ (0.5 mmol), CH_3CN (2 mL), 75 °C, CO balloon; the reaction time for the first run was 6 h, and others were 24 h.

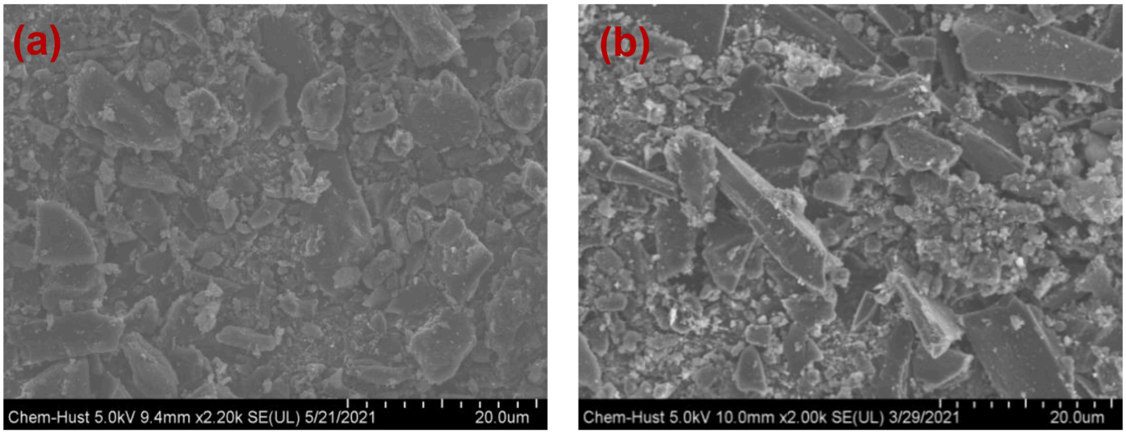


Fig. 3. The SEM images of (a) fresh and (b) 5th used Pd/C catalyst.

catalytic efficiency reduced, giving only 77%, 72% and 68% yields of bifurfural formation with less than 1% yield of dehalogenated furfural formation (Table 3, entries 4, 5 and 6), even though 5-bromofurfural could be almost completely converted (>99%) except in the case of using Na_2CO_3 as the base (86%). Using KOH and NaOH as the base provided much less efficiency, giving 13% and <1% yield of bifurfural, respectively, with >99% conversion of 5-bromofurfural (Table 3, entries 7 and 8). Clearly, a relatively weak alkaline condition is preferred for this reductive coupling reaction, which is similar to our previous studies on aqueous carbonylation of 5-bromofurfural to FDCA, [35] accordingly supporting that it is the basicity, not the solubility of the added base that affects the catalytic efficiency in the present study.

Next, the reusing capability of the commercial Pd/C catalyst was investigated for this reaction. As shown in Fig. 2, the catalyst could be reused 5 times without significant activity loss, still giving 90% conversion with 89% yield of bifurfural. The gradually reduced efficiency of catalyst was attributed to the challenges in separation of the Pd/C catalyst with the bifurfural product after the reaction. Because the solubility of the bifurfural product is quite low in CH_3CN, it makes bifurfural absorbed on the surface of the Pd/C catalyst toughly, and hard to clean up the bifurfural product in the catalyst recycling, which was evidenced from the FT-IR spectrum of recycled catalyst (Figure S2), thus disturbing the catalytic efficiency in the reusing test. As a result, after the first run, the reaction needed to be conducted in extended reaction time, that is, 24 h, to achieve the almost complete conversion of 5-bromofurfural. Fortunately, in each reusing test, the selectivity to bifurfural always retained as high as that in the first run, thus supporting the stable activity of Pd/C catalyst. Particularly, the ICP analysis of the reaction medium also revealed an ignorable Pd leaching, corresponding to <0.5% palladium loss from the Pd/C catalyst, further supporting its stability in catalysis. Additionally, in order to check the role of the leached Pd in this reductive coupling reaction, a complimentary

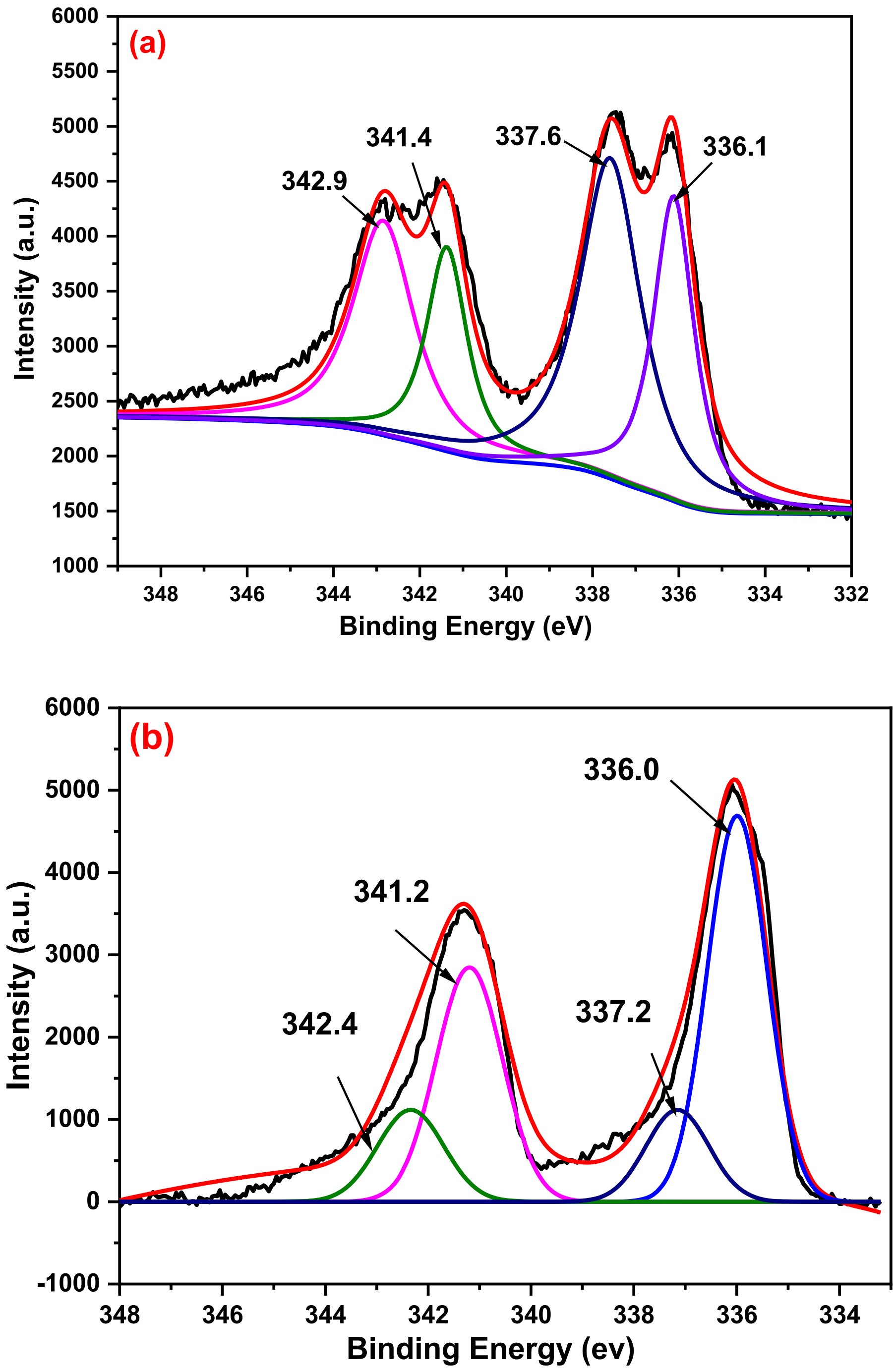


Fig. 4. The XPS characterizations of (a) fresh and (b) 5th used Pd/C catalyst.

Table 4
Porosity of the prepared poly(Schiff base) materials.

Materials[a]	S_{BET}(m^2 g^{-1})[b]	PV (cm^3 g^{-1})[c]	MPV (cm^3 g^{-1})[d]
p-PA-BF	115.2	0.75	0.004
p-PA-BB	48.5	0.28	0.004
m-PA-BF	14.6	0.006	0.006
m-PA-BB	216.2	0.43	0.05

[a] *p*-PA=*p*-phenylenediamine, *m*-PA=*m*-phenylenediamine, BF=bifurfural, BB=4,4'-bibenzyaldehyde.

[b] Surface area calculated from the nitrogen adsorption isotherm at 77.3 K using the BET equation.

[c] Total porous volume calculated from nitrogen adsorption at $P/P_0 = 0.995$.

[d] Micropore volume calculated from nitrogen adsorption at $P/P_0 = 0.05$.

Table 5
Thermal properties of the prepared poly(Schiff base) materials.

Materials[a]	T_d^5(°C)[b]	T_d^{10}(°C)[c]
p-PA-BF	406	435
p-PA-BB	514	524
m-PA-BF	107	186
m-PA-BB	117	159

[a] *p*-PA=p-phenylenediamine, *m*-PA=m-phenylenediamine, BF=bifurfural, BB=4,4'-bibenzyaldehyde.

[b] The temperature of 5% weight loss by TGA.

[c] The temperature of 10% weight loss by TGA.

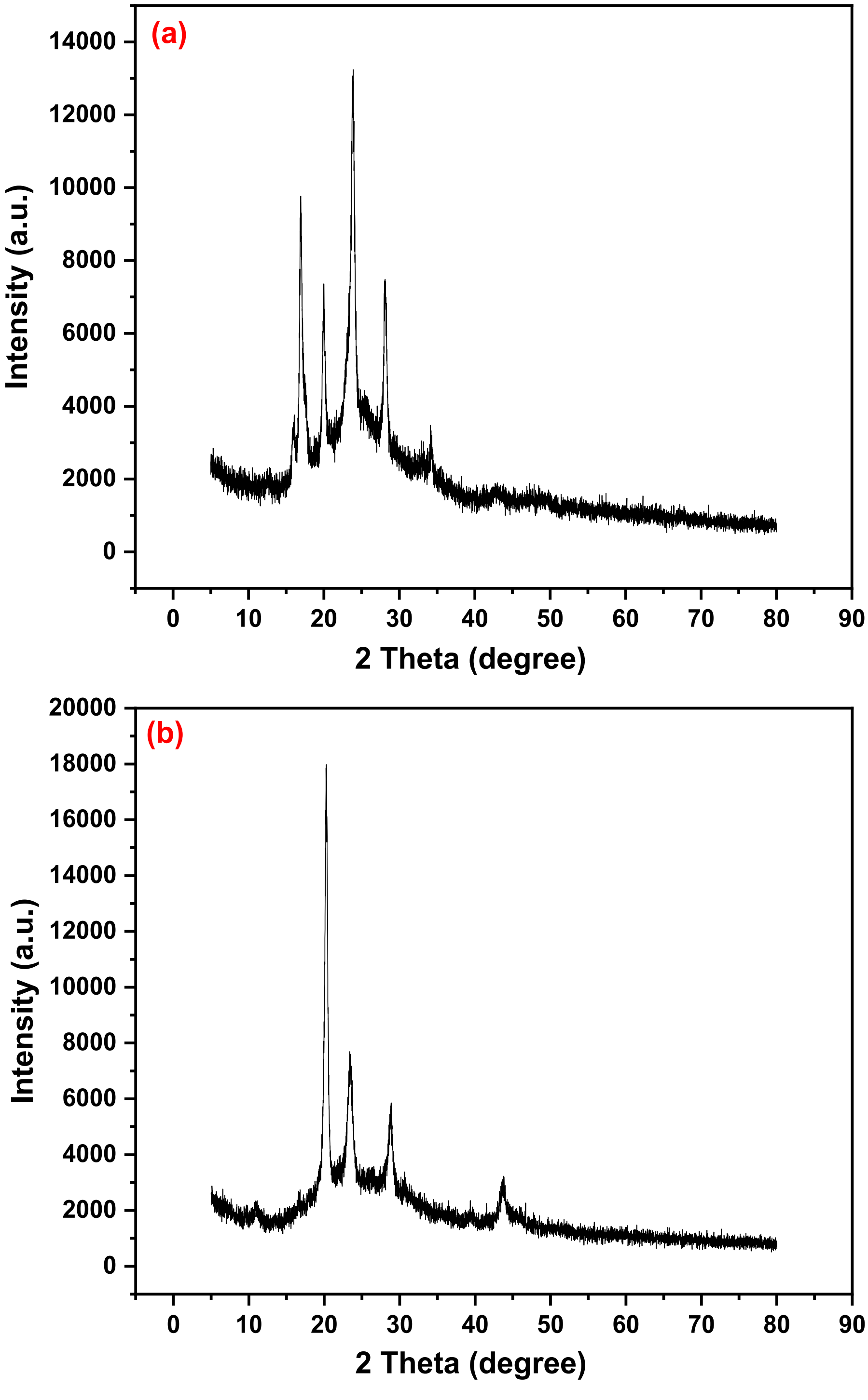


Fig. 5. The PXRD patterns of prepared poly(Schiff base) materials: (a) *p*-PA-BF; (b) *p*-PA-BB, where *p*-PA=*p*-phenylenediamine, BF=bifurfural, BB=4,4'-bibenzyaldehyde.

experiment was conducted by using the mother solution of a previous run for the next run, it was found that no bifurfural formation observed, thus excluding any homogeneous contribution to this reaction.

The stable activity of the Pd/C catalyst was also evidenced from the catalyst characterizations of the fresh and 5th used Pd/C catalyst. As shown in Fig. 3, the SEM characterizations of the fresh and 5th used Pd/C catalyst disclosed that they have a very similar morphology, indicating that the Pd/C catalyst was quite stable in catalysis, and could be reused for more cycles. The XPS characterizations of fresh Pd/C catalyst revealed two electronic energy bands of palladium species (Fig. 4), including the electronic energy peaks at 342.8 and 337.6 eV coresponding to the $3d_{3/2}$ and $3d_{5/2}$ elctron of the divalent Pd^{2+} species, and the peaks at 341. 4 and 336.1 eV corresponding to the mellatic Pd species, which are similar to those in literature. [40,55,56] The peak separation of these peaks disclosed that, in the fresh Pd/C catalyst, it contained 61.2% of the Pd^{2+} species and 38.8% of the Pd^0 species; interestingly, in the 5th used Pd/C catalyst, it was found that it contained 76.4% of the Pd^0 species with only 23.6% of the Pd^{2+} species, indicating that during the reductive coupling of 5-bromofurfural to bifurfural with CO as the reductant, the Pd^{2+} species in the Pd/C catalyst was gradually transformed to the Pd^0 species. Because the real active species for reductive dehalgenation of 5-bromofurfural is the Pd^0 species as those in literature, [34-38,39,57] such a component change from the Pd^{2+} species to the Pd^0 species did not harm the catalytic activity as shown in Fig. 2. Additionally, in the gram level synthesis starting with 1 g of 5-bromofurfural, it also provided 0.49 gram of bifurfural as the isolated product, corresponding to 90% yield. However, in the potential synthesis on a large scale with the catalyst recycling, an improved method for product separation from the Pd/C catalyst is crucial, which can avoid the disturbance of bifurfural on the activity of the catalyst, thus reducing the reaction time when using the recycled Pd/C as the catalyst.

So prepared bifurfural was next tested as a monomer to synthesize poly(Schiff base) materials through its polymerization with *p*-benzyldiamine and *m*-benzyldiamine, respectively, according to the literature, [43,48,49] and compared with the corresponding poly(Schiff base) materials from petrochemical 4,4'-biphenyldicarboxaldehyde. The FT-IR spectra of prepared polymers disclosed a relatively strong band around 1610 cm^{-1} in all of these polymers, evidencing the formation of the imine -CH=N- bond in the polymers (Figure S3). [43] The porous properties of these polymer were analyzed by nitrogen absorption/desorption analysis (Figure S4), and the data are summarized in Table 4. As shown, in polymerization with *p*-phenylenediamine, bifurfural derived poly(Schiff base) material disclosed much larger surface area than that from 4,4'-biphenyldicarboxaldehyde, that is 115.2 vs 48.5 m^2 g^{-1}. Notably, both of them had a similarly ignorable micropore volume, that is, 0.004 cm^3 g^{-1}, however, the mesopore volume of bifurfural based poly(Schiff base) was much higher than that from 4,4'-biphenyldicarboxaldehyde, that is, 0.75 vs 0.28 cm^3 g^{-1}, making its surface area much larger than that from 4,4'-biphenyldicarboxaldehyde (Table 4, entry 1 vs 2). In contrast, in the case of using *m*-phenylenediamine as the monomer, the surface area of bifurfural based poly(Schiff base) is sharply smaller than that from 4,4'-biphenyldicarboxaldehyde, that is 14.6 vs 216.2 m^2 g^{-1}, because both of its pore volume and micropore volume were smaller than those from 4,4'-biphenyldicarboxaldehyde, including 0.006 vs 0.43 cm^3 g^{-1}, and 0.006 vs 0.05 cm^3 g^{-1}, respectively (Table 4, entry 3 vs 4). Clearly, all of the surface area, pore volume and micropore volume of prepared poly(Schiff base) materials are related to the structure of the monomers, that is, the polymerization of a linear monomer with a non-linear monomer can provide the large values of these porosity parameters, whereas they are small when the materials were prepared from both linear monomers or both non-linear monomers. Especially, the poly(Schiff base) material from bifurfural and *m*-phenylenediamine, in which both of them are non-linear monomers, disclosed almost ignorable pore and micropore volumes (Table 4, entry 3). Notably, the TGA analysis of these poly(Schiff base) disclosed that, while *m*-phenylenediamine based poly(Schiff base) materials with bifurfural or 4,4'-biphenyldicarboxaldehyde are thermal unstable that continuously decomposed with the temperature elevating from room temperature, both of *p*-phenylenediamine based poly(Schiff base) materials with bifurfural and 4,4'-biphenyldicarboxaldehyde demonstrated high thermal stability (Table 5 and Figure S5). For example, poly(Schiff base) prepared from bifurfural with *p*-phenylenediamine displayed the thermal decomposition temperatures of 5% weight loss (T_d^5) and 10% weight loss(T_d^{10}) above 406 and 435°C, respectively, thus offering it a promising thermal stability in potential applications. The crystal properties of the poly(Schiff base) materials were characterized by powder X-ray diffraction (PXRD) analysis. It was observed that the geometry of the building block significantly affected the crystal properties of prepared polymers. As disclosed, the non-linear structure of *m*-phenylenediamine prohibited the space-efficient packing of the poly(Schiff base) materials in the solid state, leading to a very low crystalline behavior (Figure S6), whereas the linear structure of *p*-phenylenediamine enabled the corresponding poly(Schiff base) materials to show clear crystallinity for both bifurfural and 4,4'-bibenzyaldehyde (Fig. 5).

4. Conclusions

A simple method was explored for the synthesis of bifurfural from the furfural platform through reductive coupling 5-bromofurfural by using commercial Pd/C as the catalyst and CO as the reductant source, and it is a sustainable route in view of the carbon source required for this synthesis. So prepared bifurfural can be employed as a monomer for the synthesis of poly(Schiff base) materials which demonstrates different porosity properties from those derived from its petrochemical analogue, that is, 4,4'-biphenyldicarboxaldehyde, and their thermal stability is also very good in certain case. In view of bulk availability of furfural from raw agricultural materials, feasible synthesis of bifurfural from the furfural platform may offer it a new opportunity in new material synthesis, thus expanding its market in polymer industry.

Declaration of Competing Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of the manuscript titled.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2021.111814.

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