Tailoring the Product Distribution with Batch and Continuous Process Options in Catalytic Hydrogenation of Furfural

Narayan S. Biradar, Amol A. Hengne, Shobha N. Birajdar, Rameshwar Swami, and Chandrashekhar V. Rode*

Chemical Engineering & Process Development Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan Pune 411008, India

ABSTRACT: Various noble metal catalysts were screened in a batch operation for a furfural (FFR) single-step decarbonylation and hydrogenation reaction to obtain THF in high selectivity. Among these, the 3% Pd/C showed complete FFR conversion with a total of 80% selectivity to ring hydrogenated products including tetrahydrofuran (THF). The order of activity exhibited by other noble metals was Pt/C > Re/C > Ru/C. Although Pt/C exhibited the highest activity, its decarbonylation and ring hydrogenation ability were the least (24%) with a major product selectivity of 66% to furfuryl alcohol (FAL). Similarly, the Cu catalyst gave almost complete selectivity to FAL. In a continuous operation (23 g catalyst bed), the 3% Pd/C catalyst showed higher selectivity of >40% compared to THF alone with complete FFR conversion and on-stream activity of ~100 h. The reaction pathway elucidated from some control experiments revealed that the decarbonylation of FFR to furan over the Pd/C catalyst is a prerequisite for THF formation.

1. INTRODUCTION

Utilization of biomass has received a lot of attention for the development of a sustainable society. Paradigm change from fossil to biomass resources for the manufacture of commodity and fine chemicals will become inevitable in the near future because biomass is the only renewable source of carbon.¹ Lignocellulosic biomass is a more promising feedstock for downstream applications as it is more abundant, cheaper, and potentially more sustainable.² The acid hydrolysis of pentose sugars followed by dehydration evolving three water molecules gives furfural (C5 molecule).³ Furfural (FFR) is one of the most appropriate platform molecules for the production of a variety of value added chemicals and fuels such as furan, furfuryl alcohol (FAL), tetrahydrofurfuryl alcohol (THFAL), 2-methyl furan (MF), 2-methyl tetrahydrofuran (MTHF), and tetrahydrofuran (THF).⁴ All these products are industrially important; however, their distribution in FFR hydrogenation primarily depends on reaction conditions and the catalyst, both of which can be suitably tailored to suit the requirement.⁵ Among several products of FFR hydrogenation, THF and other ring hydrogenated products are of seminal interest commercially and more so if obtained in a single-step conversion of FFR. These products have versatile applications as industrial solvents, as monomers, etc. One of these products, THF, can be produced by decarbonylation of furfural to furan under reductive conditions and then subsequently hydrogenated to THF. Conventionally, THF can be produced by a number of different routes, the major ones include dehydration of 1,4butanediol (BDO) and hydrogenation of maleic anhydride, both of which are dependent on fossil feedstock and multistep processes involving use of reagents, heavy metal complexes, and harsh reaction conditions.⁶ These drawbacks can be easily overcome by a single-step selective hydrogenation of FFR derived from biorenewable feedstock. Since the single-step formation of THF from FFR involves decarbonylation as well

as ring hydrogenation steps in a tandem way, an appropriate combination of a catalyst system and reaction conditions needs to be developed in order to achieve the highest selectivity to THF.

Although several supported noble (Pt, Pd, Ru, Rh, Pd) and non-noble (Cu, Ni) metals have been reported for the hydrogenation of FFR, the major product of hydrogenation is furfuryl alcohol. A 5% Pt/C catalyst has been found to give 58% FFR conversion and >98.5% selectivity to FAL at 403-448 K and 10-20 bar H₂ pressure.^{5c} Non-noble metal catalysts included Raney nickel and Cu, mainly used for FFR hydrogenation to FAL showing the highest selectivity of >98% to FAL with conversion in the range of 65 to 99%.⁷ Poliakoff and his group reported a twin catalyst system (Cu and Pd/C) for the continuous conversion of FFR to a variety of products at different reaction temperatures, which included FAL, THFAL, MeTHF, MeTHF, and furan at 393-523 K reaction temperature.⁸ Sethissa and Resasco studied different silica-supported metal catalysts for the hydrogenation of FFR among which 1% Pd/SiO₂ gave 20% THF with 69% conversion in a continuous fixed-bed reactor.⁹ Using microreactor system, 80% (mol %) selectivity to THF was achieved with 90% (mol %) conversion of FFR over carbon-supported Pd NPs.¹⁰ In the case of the Pd/Al₂O₃ catalyst, K-doping was effective for decarbonylation of FFR with complete conversion, but almost complete selectivity (>99%) was obtained with an unsaturated product, furan.¹¹

In our work on FFR hydrogenation, while screening several catalysts, total selectivity of 70% was achieved for ring hydrogenated products including THF over the 3% Pd/C catalyst. THF selectivity enhanced 2-fold at complete

Special Issue: Continuous Processes 14

Received:June 18, 2014Published:August 7, 2014

Organic Process Research & Development

conversion of FFR when the hydrogenation was performed in a continuous mode. THF selectivity could be tuned by manipulating the process parameters in both batch and continuous operations.

2. EXPERIMENTAL SECTION

2.1. Material. Furfural (99%) and activated charcoal were purchased from Sigma-Aldrich, Bangalore, India, while sodium hydroxide (NaOH), sodium borohydride (NaBH₄), and isopropyl alcohol were purchased from Thomas Baker, India. Palladium chloride (PdCl₂) was purchased from Lab-India. Hydrogen gas of high purity (99.99%) was obtained from Inox, India.

2.2. Catalyst Preparation. Supported Pd, Pt, Ru, and Re catalysts were prepared by a wet-impregnation method. In a typical preparation of the 3% Pd/C catalyst, 0.159 g of PdCl₂ was dissolved in a minimum amount of dilute hydrochloric acid, ensuring the complete dissolution of the precursor. Under stirring, 2 g of a slurry of carbon support prepared in water was added to the above solution, and solution was stirred for 2 h at room temperature. After 1 h, 10 M sodium hydroxide solution was added under stirring to make the resultant pH = 7-8, and the stirring was continued for another 30 min. After that, 3 mL formaldehyde was added under stirring as a reducing agent. The reaction mixture was further stirred for 30 min and was then cooled and filtered to obtain the catalyst, which was dried at 373 K. Similarly, other catalysts screened for hydrogenation of furfural were prepared using the same procedure.

2.3. Catalyst Characterization. BET surface area and N_2 adsorption isotherms of all Pd-supported catalysts were obtained along with the pore size distribution calculated using the DFT method on a Quantachrome QuadraWi (5.02 version). Particle size was studied by transmission electron microscopy (HR-TEM) on a JEOL 1200 EX model. For this purpose, a small amount of the solid sample was sonicated in 2-propanol for 1 min. A drop of the prepared suspension was deposited on a Cu grid coated with a carbon layer, and the grid was then dried at room temperature before analysis.

2.4. Catalyst Activity. The performance of the prepared catalyst was tested in both batch as well as continuous operations.

Batch reactions were carried out in a 300 mL capacity autoclave supplied by Parr Instruments Co. USA. The typical hydrogenation conditions were as follows: temperature, 473–513 K; hydrogen pressure, 20–50 bar; furfural concentration, 5 wt %; solvent, 95 mL; agitation speed, 1000 rpm; and catalyst loading, 0.5 g.

Continuous hydrogenation of furfural was carried out in a bench scale, high-pressure, fixed-bed reactor supplied by M/s Geomechanique, France. This reactor setup consisted of a stainless steel single tube of 0.34 m length and 1.5×10^{-2} m inner diameter. The reactor was heated by two tubular furnaces whose zones (TIC1 and TIC2) were independently controlled at the desired bed temperature. The reactor was provided with mass flow controllers, pressure indicator, and controller (PIC) devices and two thermocouples to measure the temperature at two different points. A storage tank was connected to the HPLC pump through a volumetric burette to measure the liquid flow rate. The pump had a maximum capacity of 3 \times 10^{-4} m³/h under a pressure of 100 bar. The gas-liquid separator was connected to the other end of the reactor through a condenser. Ten grams of catalyst was charged into the reactor. The section of 7×10^{-2} m above and 7×10^{-2} m

below the catalyst bed was packed with carborandum as an inert packing, and the remaining reactor was filled with catalyst powder in four sections which were separated by carborandom. Before the actual experiment was started, the reactor was flushed thoroughly, first with N_2 and then with H_2 at room temperature. Then the reactor was pressurized with H₂ after attaining the desired temperature. The liquid feed was "switched on" after the reactor reached the operating pressure and was kept at that value for 1 h to obtain the constant liquid flow rate. Liquid samples withdrawn time to time during the reaction were analyzed with a Trace GC 700 series GC System (Thermo SCIENTIFIC) coupled with an FID detector and a capillary column (HP-5 capillary column, 30 m length \times 0.32 mm i.d.). The following temperature programme was used for GC analysis: 40 °C (3 min), 1 °C/min, 45 °C (1 min), 10 °C/ min, 60 °C (0 min), 20 °C/min, 25 °C (1 min). Several experiments were carried out at different inlet conditions of liquid and gas flow rates and in the temperature and pressure ranges of 423-513 K and 20-50 bar, respectively. Steady-state performance of the reactor was observed by analysis of the reactant and products in the exit stream.

The conversion and selectivity were calculated as follows:

(%) conversion

$$= \frac{\text{initial moles of furfural} - \text{final moles of furfural}}{\text{initial moles of furfural}} \times 100$$
(1)

(%) selectivity =
$$\frac{\text{moles of product formed}}{\text{moles of furfural consumed}} \times 100$$
 (2)

3. RESULTS AND DISCUSSION

This study was mainly focused on (i) identifying a catalyst for single-step decarbonylation followed by ring hydrogenation of furfural and studying the product distribution in a batch reactor; (ii) evaluating time on stream (TOS) activity and product distribution of the best catalyst for continuous furfural hydrogenation; (iii) optimizing the reaction conditions and approach for batch and continuous reaction to achieve the highest selectivity to intermediate furan and THF via decarbonylation and hydrogenation.

3.1. Catalyst Characterization. Textural properties of all the Pd-supported catalysts are shown in Table 1 from which it

Table 1. Characterization of Pd-Supported Catalysts

	catalyst				
characterization	3% Pd/C	3% Pd/SiO ₂	3% Pd/CaCO ₃		
BET surface area	639.8 m ² /g	$135.3 \text{ m}^2/\text{g}$	231.4 m ² /g		
pore size	6 Å	65–85 Å	35 Á		
particle size	4-5 nm	10-15 nm	8-9 nm		

was clear that the surface area of the carbon-supported catalyst was the highest ($613 \text{ m}^2/\text{g}$), and the CaCO₃- and silicasupported catalysts showed lower surface areas of 231.4 and 135.3 m²/g, respectively. N₂ physisorption studies showed type-I and type-IV adsorption isotherms for all the supported Pd catalysts. The 3% Pd/C catalyst showed microporous nature, while the 3% Pd/SiO₂ and 3% Pd/CaCO₃ showed meso/ macroporous nature. HR-TEM characterization of the 3% Pd/ C catalyst also showed an excellent dispersion of palladium particles on the carbon support without any agglomeration as

			selectivity %						
run	catalyst	conversion %	FAL	THF	THFAL	MF	MTHF	pentanediol	furan
1	3% Pd/C	100	16	20	32	14	18	0	
2	3% Pd/SiO ₂	75.5	52	3	37	<1	<1	6	
3	3% Pd/CaCO ₃	91.5	21	0	49	15	16		
4	3% Pt/C	89.3	66	0	23	10	1		
5	3% Ru/C	57.3	31	0	40	17	12		
6	3% Re/C	71.78	23	0	23	45	10		
7	CuAl	100	>99.5	0	<0.5	0	0		

^aReaction conditions: furfural, 5% (w/w); solvent, isopropyl alcohol (95 mL); temperature, 493 K; H₂ pressure, 35 bar; agitation speed, 1000 rpm; catalyst (3% Pd/C), 0.5 g; reaction time, 5 h.

the average particle size was found to be 4-5 nm, determined by counting about 50 individual particles.

3.2. Catalyst Screening. *Batch Operation.* The results of screening various catalysts for the decarbonylation—hydrogenation of furfural are summarized in Table 2. In our previous studies, Pd/MFI was found to be the best catalyst for FFR hydrogenation, however, with the highest selectivity to THFAL formed by ring hydrogenation without decarbonylation.¹² Hence, initially, Pd catalysts on supports other than MFI were explored, and interestingly, it was found that the 3% Pd/C gave complete FFR conversion with 20% selectivity to THF, which has been the highest reported so far. The total selectivity to ring hydrogenated products (THF, THFAL, and MTHF) achieved was as high as 80% (entry 1, Table 2). Figure 1 shows



Figure 1. CT profile of FFR hydrogenation over 3% Pd/C catalyst. Reaction conditions: furfural, 5% (w/w); solvent, isopropyl alcohol (95 mL); H_2 pressure, 35 bar; agitation speed, 1000 rpm; catalyst (3% Pd/C), 0.5 g; reaction time, 5 h.

the reaction profile in terms of FFR conversion and simultaneous formation of THF along with other products (FAL, MF, THFAL, and MTHF) as a function of reaction time, over the 3% Pd/C catalyst. This indicates that the decarbonylation and hydrogenation of FFR took place from the start of the reaction. However, initially, THF selectivity was 12% which after 1 h increased to 20% in 5 h along with an increase in selectivity to other ring hydrogenated products such as THFAL (34%) and MTHF (20%) at the cost of FAL and MF. The order of activity for three supports for the obtained Pd catalyst was Pd/C > Pd/CaCO₃> Pd/SiO₂. The selectivity to THF was the highest for carbon support due to higher surface area and metal dispersion and smaller particle size compared to those of

other supports. In case of Pd/SiO₂ catalyst, the major product formed was FAL (entry 2, Table 2) with ~40% of ring hydrogenated products. Although Pd/CaCO3 showed ~92% FFR conversion, surprisingly, no formation of any THF was observed (entry 3, Table 2). As carbon was found to be the best support for the Pd catalyst, other noble metals such as Pt, Ru, and Re with the same loading of 3% on carbon were also evaluated for FFR hydrogenation. However, all three metal functions showed performance inferior to that of Pd, and the order of activity among them was found to be Pt/C > Re/C >Ru/C. Although Pt/C exhibited the highest activity, its ring hydrogenation ability was the least (24%), with a major product selectivity of 66% to FAL (entry 4, Table 2). Ru/C showed significant formation of ring hydrogenated products (52%, entry 5, Table 2), while the Re/C catalyst gave a total selectivity of 34% to ring hydrogenation (entry 6, Table 2). Contrary to our expectation, none of the noble metals other than Pd showed any selectivity to THF. A non-noble metal catalyst tested was CuAl that showed complete conversion of FFR with the highest selectivity to a single product, that is, furfuryl alcohol >99.5% (entry 7, Table 2) which was in accordance with Cu-Cr catalysts.

As only the Pd/C catalyst showed the highest activity for FFR conversion with the highest selectivity to ring hydrogenated products (>70%) and to THF as high as 20% in a single step, the reaction pathway for FFR hydrogenation was also studied by some control experiments. The experiment with FFR was conducted by replacing H₂ with N₂ under the same reaction conditions that gave complete conversion of FFR with >99% selectivity to furan, confirming that the decarbonylation of FFR over the Pd/C catalyst is a prerequisite for THF formation. The results of hydrogenation experiments with various FFR hydrogenation products as substrates over the 3% Pd/C catalyst are shown in Table 3. With FAL as a substrate, complete selectivity to ring hydrogenation product THFAL was obtained, indicating that the side chain hydrogenation/ decarbonylation did not proceed via THFAL (entry 2, Table 3). This was also confirmed when THFAL itself was used as a starting material (entry 3, Table 3). Similarly, hydrogenation of 2-methyl furan and furan gave complete selectivity to MTHF and THF, respectively, thus establishing efficient ring hydrogenation over the Pd/C catalyst under the conditions of the present work. Based on these results, the proposed reaction pathway is shown in Scheme 1. In summary, furfuryl alcohol can be selectively obtained by the use of Cu-based catalysts under mild reduction conditions, while with noble metal catalysts, Pd/C was particularly effective for decarbonylation to give furan that can be subsequently hydrogenated to THF.

Table 3. Hydrogenation of Different Substrates^a

Compound	Conversion, %	Selectivity, %						
		FA	THF	THFAL	MF	MTHF	Pentanediol	Furan
Furfural	100	12	20	32	10	18	8	
OH Furfuryl alcohol	100	SM		100				
OH TetrahydroFurfuryl alcohol				SM				
Methyl Furan	100				SM	100		
Furan	100		100					SM

^{*a*}Reaction conditions: substrate, 5% (w/w); solvent, isopropyl alcohol (95 mL); temperature, 493 K; H_2 pressure, 35 bar; agitation speed, 1000 rpm; catalyst (3% Pd/C), 0.5 g; reaction time, 5 h.

Scheme 1. General Reaction Pathway for Furfural Hydrogenation





As 3% Pd/C catalyst showed the excellent performance for hydrogenation of FFR with the highest selectivity to ring hydrogenated products along with THF, further optimization of reaction conditions was done over the same catalyst in batch as well as continuous operations, and the results are discussed below.

3.2.1. Effect of Agitation Speed. In order to check the external mass transfer resistances, the effect of agitation speed was studied in the range of 500 to 1000 rpm, keeping all other reaction parameters the same, and the results are shown in Figure 2. The complete conversion of FFR was observed

Figure 2. Effect of agitation speed. Reaction conditions: furfural, 5% (w/w); solvent, isopropyl alcohol (95 mL); temperature, 493 K; catalyst (3% Pd/C), 0.5 g; reaction time, 5 h.

irrespective of the agitation speed variation from 500 to 1000 rpm, indicating clearly that the external mass transfer did not play any significant role under the conditions of the present work. Interestingly, selectivity to THF slowly increased from 15 to 20% with an increase in the agitation speed from 500 to 1000 rpm. Along with THF, other ring hydrogenated products formed were about 52–55%. All of the studies were then carried out at the agitation speed of 1000 rpm.



Figure 3. Effect of temperature. Reaction conditions: furfural, 5% (w/w); solvent, isopropyl alcohol (95 mL); H_2 pressure, 35 bar; agitation speed, 1000 rpm; catalyst (3% Pd/C), 0.5 g; reaction time, 5 h.

selectivity to THF increased from 13 to 20% with increasing H_2 pressure from 20 to 35 bar with almost complete conversion of FFR. While increasing H_2 pressure beyond 35 bar, selectivity to pentanediols increased up to 6% and that to other ring hydrogenated products was found to be in the range of 50–55%. The increase in selectivity to THF (22%) at high H_2 pressure and other ring hydrogenated products was due to higher surface concentration of hydrogen.

3.2.3. Effect of Temperature. The effect of temperature on FFR conversion and product distribution was studied in the range of 473–513 K by keeping all other parameters the same. Figure 4 shows that the selectivity to THF increased from 15 to



Figure 4. Effect of hydrogen pressure. Reaction conditions: furfural, 5% (w/w); solvent, isopropyl alcohol (95 mL); agitation speed, 1000 rpm; catalyst (3% Pd/C), 0.5 g; reaction time, 5 h.

20% as the temperature increased from 473 to 493 K; however, further increase in temperature from 493 to 513 K marginally influenced the THF selectivity (21%), but the further hydrogenation product, pentanediol, was formed to the extent of 6%. Along with THF, other ring hydrogenated products formed were 53-54%. Thus, both decarbonylation and ring hydrogenation reactions were favored at higher temperature.

3.2.4. Effect of Catalyst Concentration. The effect of catalyst concentration on the conversion of furfural and selectivity to THF was also studied in the range of 0.250-0.750 g at 493 K and 35 bar H₂ pressure, and the results are shown in Figure 5. It was found that as the catalyst loading



Figure 5. Effect of catalyst concentration. Reaction conditions: furfural, 5% (w/w); solvent, isopropyl alcohol (95 mL); temperature, 493 K; H₂ pressure, 35 bar; agitation speed, 1000 rpm; reaction time, 5 h.

increased from 0.25 to 0.75 g, selectivity to THF increased from 14 to 22%. The increase in THF selectivity was mainly due to the increase in number of catalytic active sites with increasing catalyst concentration at constant FFR loading.

3.2.5. Effect of Pd Metal Loading. As Pd was the active metal function for both hydrogenation and decarbonylation in FFR conversion to THF, the effect of its loading on carbon support on selectivity of THF was studied, and the results are shown in Figure 6. For this purpose, Pd loading was varied in the range of 1 to 5%, and it was found that the conversion of FFR remained constant (100%) for all the metal loadings, while the selectivity to THF increased from 10 to 20% as the metal loading increased from 1 to 3%. At a higher metal loading of 5%, the selectivity to THFAL and pentanediols increased at the cost of THF, which decreased to 14%. At higher Pd loading,



Figure 6. Effect of Pd metal loading. Reaction conditions: furfural, 5% (w/w); solvent, isopropyl alcohol (95 mL); temperature, 493 K; H_2 pressure, 35 bar; agitation speed, 1000 rpm; catalyst, 0.5 g; reaction time, 5 h.

Organic Process Research & Development

hydrogenation reactions were apparently faster than the decarbonylation reaction, resulting in lowering the THF selectivity.

3.2.6. Effect of Furfural Concentration. In order to achieve maximum productivity for FFR hydrogenation, the effect of substrate concentration on conversion and selectivity was studied and the results are shown in Figure 7. With an increase



Figure 7. Effect of furfural concentration. Reaction conditions: solvent, isopropyl alcohol (95 mL); temperature, 493 K; H_2 pressure, 35 bar; agitation speed, 1000 rpm; catalyst (3% Pd/C), 0.5 g; reaction time, 5 h.

in concentration of FFR from 5 to 20 wt %, its conversion drastically decreased from 100 to 70% accompanied by huge decrease of 10-fold in THF selectivity (2%). This was mainly due to the unconverted intermediates, furan (35%) and FAL (35%). Interestingly, furan and FAL are the intermediates of two different reactions, decarbonylation and side chain hydrogenation. This means that the ring hydrogenation was drastically affected by higher substrate loading that was responsible for the higher extent of coverage of active sites required for ring hydrogenation. This result also suggests that the hydrogenation of the FFR to THF pathway is via decarbonylation of FFR to furan followed by its ring hydrogenation to THF (Scheme 1).

3.2.7. Catalyst Recycle Study. To check reproducibility and stability of the 3% Pd/C catalyst after the first hydrogenation experiment, the reaction crude was allowed to settle down and the clear supernatant product mixture was separated out. To the catalyst remaining in the reactor was added fresh charge, and the subsequent hydrogenation run was continued. This procedure was followed for four subsequent runs, and the results are shown in Figure 8. Our 3% Pd/C catalyst showed almost complete conversion of FFR with consistent selectivity to THF and all other remaining products as that of the fresh catalyst even after the fourth reuse.

3.2.8. Decarbonylation Followed by Hydrogenation. It was observed from Table 3 that the ring hydrogenation of furan directly gives THF. Hence, FFR to THF via decarbonylation (Scheme 1) followed by the ring hydrogenation pathway could be more facile. This was evidenced by a control experiment in which concentration versus time profile for decarbonylation of FFR to furan in N_2 atmosphere was studied. In this case, almost complete conversion of FFR with selective formation of furan was achieved (Figure 9). In the same experiment after complete conversion of furfural, nitrogen was replaced by hydrogen and



Figure 8. Catalyst recycle study. Reaction conditions: furfural, 5% (w/w); solvent, isopropyl alcohol (95 mL); temperature, 493 K; H_2 pressure, 35 bar; agitation speed, 1000 rpm; catalyst (3% Pd/C), 0.5 g; reaction time, 5 h.



Figure 9. Decarbonylation followed by hydrogenation. Reaction conditions: furfural, 5% (w/w); solvent, isopropyl alcohol (95 mL); temperature, 493 K; H_2 pressure, 35 bar; agitation speed, 1000 rpm; catalyst (3% Pd/C), 0.5 g; reaction time, 5 h.

the reaction was continued. Selective formation of THF was observed due to ring hydrogenation of furan; however, furan conversion was restricted to only 40%, due to poisoning of active Pd sites by CO formed during the decarbonylation reaction.

Continuous Operation. As discussed above, the 3% Pd/C was established as the best catalyst for direct FFR conversion to THF and other ring hydrogenated products. The same catalyst was therefore evaluated for its time on stream activity in a continuous operation over a bed of catalyst packed in a single tube reactor, and the results are shown in Figure 10. Complete conversion of FFR was achieved consistently over a period of 100 h, and very interestingly, the selectivity to THF enhanced by 2-fold (20 to 41%) as compared to the batch operation, while other ring hydrogenated products comprised 36% THFAL and 7% MTHF. As TOS increased, catalyst was exposed to hydrogen at the reaction temperature for a longer duration of time, resulting in its continuous in situ activation. This might have significantly contributed to the higher extent of ring hydrogenation, resulting in enhanced THF selectivity. This



Figure 10. Continuous reaction. Reaction conditions: catalyst (3% Pd/C), 10 g; solvent, isopropyl alcohol; 5 wt % furfural; feed flow rate, 30 mL/h; H_2 flow rate, 10 Nl/h; H_2 pressure, 35 bar; temperature, 493 K.

Time, h

TOS performance of the 3% Pd/C catalyst giving THF with as much as >40% selectivity becomes an excellent process option for direct conversion of biorenewable FFR to value added THF and other ring hydrogenation products from furfural. From a scale-up point of view, the effects of various reaction parameters on conversion and selectivity patterns are discussed below. These studies were conducted in a single continuous run after establishing the TOS of the catalyst for more than 100 h. Each parameter effect was continued for 24 h under steady-state conditions, and a standard run was conducted after every 24 h to ensure the original activity of the catalyst.

3.2.9. Effect of Hydrogen Pressure. Figure 11 shows the effect of hydrogen pressure on continuous hydrogenation of



Figure 11. Effect of hydrogen pressure. Reaction conditions: catalyst (3% Pd/C), 10 g; solvent, isopropyl alcohol; 5 wt % furfural; feed flow rate, 30 mL/h; H_2 flow rate, 10 Nl/h; temperature, 493 K.

FFR at 493 K. FFR conversion was found to be consistent for the H₂ pressure range of 20–50 bar studied in this work. The selectivity to THF increased appreciably from 31 to 41% with other major ring hydrogenated products such as THFAL and MTHF up to 52%, with an initial increase in the H₂ pressure from 20 to 35 bar. Thus, total selectivity to ring hydrogenated products was >90%. Selectivity to THF remained constant at 41% with further increase in H₂ pressure to 50 bar. 3.2.10. Effect of Temperature. Effect of reaction temperature on conversion and selectivity in FFR hydrogenation was studied at 35 bar H_2 pressure, and the results are summarized in Figure 12. Complete conversion of FFR was obtained for the



Figure 12. Effect of temperature. Reaction conditions: catalyst (3% Pd/C), 10 g; solvent, isopropyl alcohol; 5 wt % furfural; feed flow rate, 30 mL/h; H₂ flow rate, 10 Nl/h; pressure, 35 bar.

temperatures in a range of 473 to 493 K. Similar to the H_2 pressure effect, the extent of enhancement in selectivity to THF as well as to THFAL and MTHF was observed. There was no appreciable change observed in THF selectivity with further increase in temperature to 513 K.

3.2.11. Effect of Liquid Flow Rate. To achieve the optimum productivity in FFR hydrogenation, the effect of liquid flow rate on conversion was studied in the range of 30-60 mL/h, under constant temperature, H₂ pressure, and gas flow rate conditions, and the results are shown in Figure 13. Although



Figure 13. Effect of liquid flow rate. Reaction conditions: catalyst (3% Pd/C), 10 g; solvent, isopropyl alcohol; 5 wt % furfural; pressure, 35 bar; H_2 flow rate, 10 Nl/h; temperature, 493 K.

conversion of FFR remained constant (>99%), the selectivity to THF dramatically decreased from 41 to 17%, with an increase in feed flow rate from 30 to 60 mL/h. The decrease in THF selectivity was mainly due to accumulation of unconverted furan (24%). Furan formed in the first step of decarbonylation could not be hydrogenated in the following step due to decreasing contact time at higher liquid flow rate. At a lower liquid flow rate, the intermediate furan readily converted to THF, which is consistent with the results obtained in a batch operation.

3.2.12. Effect of Furfural Concentration. The effect of furfural concentration on continuous hydrogenation of FFR was also studied in the range of 5-20 wt % furfural, and the results are shown in Figure 14. Similar to the results observed



Figure 14. Effect of furfural concentration. Reaction conditions: catalyst (3% Pd/C), 10 g; solvent, isopropyl alcohol; feed flow rate, 30 mL/h; H₂ flow rate, 10 Nl/h; H₂ pressure, 35 bar; temperature, 493 K.

in a batch operation, higher loading of FFR concentration directly resulted in decrease in selectivity to THF (from 41 to 21%) while selectivity to the intermediate product furan was enhanced up to 30%. This was accompanied by lowering in selectivity to the ring hydrogenated products (THFAL, MTHF) as compared to the selectivity to their unsaturated precursor intermediates (FAL, MF), indicating the retardation of hydrogenation rates at higher substrate loading.

4. CONCLUSION

Single-step furfural (FFR) decarbonylation and hydrogenation over the 3% Pd/C catalyst was carried out in a continuous operation for a period of 100 h, which gave as much as 2-fold higher selectivity to THF than that in a batch operation. Product distribution studies in a batch operation showed 20% selectivity to THF, and the total selectivity to ring hydrogenated products (THF, THFAL, and MTHF) achieved was as high as 80%. FFR conversion under inert conditions (N_2) gave >99% selectivity to furan, confirming that the decarbonylation of FFR over the Pd/C catalyst is a prerequisite for THF formation. In a continuous operation, complete conversion of FFR was achieved consistently over a period of 100 h, and very interestingly, the selectivity to THF enhanced from 20 to 41% as compared to the batch operation, while other ring hydrogenated products comprised 36% THFAL and 7% MTHF. Study of the effect of process conditions in a continuous operation revealed that the total selectivity to ring hydrogenated products increased appreciably to >90%, in which THF was 41% with the initial increase in the H₂ pressure from 20 to 35 bar. On the contrary, with an increase in both liquid feed rate and furfural concentration, lower THF selectivity was obtained due to suppression of ring hydrogenation of the intermediate, furan. Thus, TOS performance of the 3% Pd/C catalyst, giving THF in as much as >40% selectivity, becomes an excellent process option for direct

conversion of biorenewable FFR to value added THF and other ring hydrogenation products from furfural.

AUTHOR INFORMATION

Corresponding Author

*E-mail: cv.rode@ncl.res.in. Tel: 020-25902349.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

One of the authors (N.S.B.) acknowledges the Council of Scientific and Industrial Research, New Delhi, for its financial support of this work under the NMITLI program (TLP 002926).

ABBREVIATIONS

FFR = furfural THF = tetrahydrofuran FAL = furfuryl alcohol THFAL = tetrahydrofurfuryl alcohol

REFERENCES

(1) (a) Huber, G. W.; Iborra, S.; Corma, A. Chem. Rev. 2006, 106, 4044–4098. (b) Corma, A.; Iborra, S.; Velty, A. Chem. Rev. 2007, 107, 2411–2502. (c) Bozell, J. J.; Petersen, G. R. Green Chem. 2010, 12, 539–554. (d) Perego, C.; Ricci, M. Catal. Sci. Technol. 2012, 2, 1776–1786.

(2) (a) Chheda, J. N.; Roman-Leshkov, Y.; Dumesic, J. A. Green Chem. 2007, 9, 342–350. (b) Xing, R.; Subrahmanyam, A. V.; Olcay, H.; Qi, W.; Walsum, G. P.; Pendse, H.; Huber, G. W. Green Chem. 2010, 12, 1933–1946. (c) Dutta, S.; De, S.; Saha, B.; Alam, Md. I. Catal. Sci. Technol. 2012, 2, 2025–2036.

(3) (a) Stein, T.; Grande, P. M.; Leitner, W.; de Maria, P. D. ChemSusChem 2011, 4, 1592–1594. (b) Sahu, R.; Dhepe, P. L. ChemSusChem 2012, 5, 751–761. (c) Hu, X.; Lievens, C.; Li, C. Z. ChemSusChem 2012, 5, 1427–1434. (d) Karinen, R.; Vilonen, K.; Niemela, M. ChemSusChem 2011, 4, 1002–1016. (e) Weingarten, R.; Cho, J.; Conner, W. C., Jr.; Huber, G. W. Green Chem. 2010, 12, 1423–1429.

(4) (a) Rodiansono; Khairi, S.; Hara, T.; Ichikuni, N.; Shimazu, S. *Catal. Sci. Technol.* **2012**, *2*, 2139–2145. (b) Nakagawa, Y.; Nakazawa, H.; Watanabe, H.; Tomishige, K. *ChemCatChem* **2012**, *4*, 1791–1797. (c) Agirrezabal-Telleria, I.; Requies, J.; Guemez, M. B.; Arias, P. L. *Green Chem.* **2012**, *14*, 3132–3140. (d) Zheng, H. Y.; Zhua, Y. L.; Teng, B. T.; Bai, Z. Q.; Zhang, C. H.; Xiang, H. W.; Li, Y. W. J. Mol. *Catal. A: Chem.* **2006**, *246*, 18–23. (e) Yang, Y.; Hu, C. W.; Abu-Omar, M. M. *ChemSusChem* **2012**, *5*, 405–410. (f) Hu, L.; Zhao, G.; Hao, W.; Tang, X.; Sun, Y.; Lin, L.; Liu, S. RSC Adv. **2012**, *2*, 11184–11206.

(5) (a) Lange, J. P.; van der Heide, E.; van Buijtenen, J.; Price, R. ChemSusChem 2012, 5, 150–166. (b) Zheng, H. Y.; Zhu, Y. L.; Bai, Z. Q.; Huang, L.; Xiang, H. W.; Li, Y. W. Green Chem. 2006, 8, 107–109.
(c) Vaidya, P. D.; Mahajani, V. V. Ind. Eng. Chem. Res. 2003, 42, 3881–3885.

(6) (a) Schoedel, N.; Haidegger, E.; Hofmann, K. H.; Patent Application US 6204399 B1, 2001. (b) Miya, B. Patent Application US 3894054, 1975. (c) Jenkins, C. L., Jr. Patent Application US 4124600, 1978.

(7) Baijun, L.; Lianhai, L.; Bingchun, W.; Tianxi, C.; Iwatani, K. Appl. Catal., A 1998, 171, 117–122.

(8) Stevens, J. G.; Bourne, R. A.; Twigg, M. V.; Poliakoff, M. Angew. Chem., Int. Ed. 2010, 49, 8856–8859.

(9) Sitthisa, S.; Resasco, D. E. Catal. Lett. 2011, 141, 784-791.

(10) Garcia-Suarez, E. J.; Balu, A. M.; Tristany, M.; Garcia, A. B.; Philippot, K.; Luque, R. *Green Chem.* **2012**, *14*, 1434–1439.

(11) Zhang, W.; Zhu, Y.; Niua, S.; Li, Y. J. Mol. Catal. A: Chem. 2011, 335, 71–81.

(12) Biradar, N. S.; Hengne, A. M.; Birajdar, S. N.; Niphadkar, P. S.; Joshi, P. N.; Rode, C. V. ACS Sustainable Chem. Eng. 2014, 2, 272– 281.

(13) Nagaraja, B. M.; Padmasri, A. H.; Seetharamulu, P.; Reddy, K. H. P.; Raju, B. D.; Rama Rao, K. S. J. Mol. Catal. A: Chem. 2007, 278, 29–37.