ACS Sustainable Chemistry & Engineering

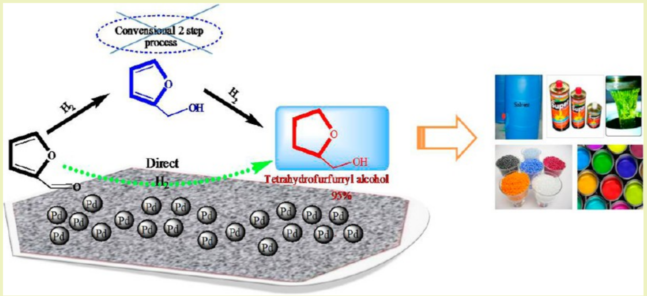
Research Article

pubs.acs.org/journal/ascecg

Single-Pot Formation of THFAL via Catalytic Hydrogenation of FFR Over Pd/MFI Catalyst

Narayan S. Biradar,[†] Amol M. Hengne,[†] Shobha N. Birajdar,[†] Prashant S. Niphadkar,[‡] Praphulla N. Joshi,[‡] and Chandrashekhar V. Rode*,[†]

[†]Chemical Engineering and Process Development Division and [‡]Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune 411008, India



ABSTRACT: Furfural (FFR) was selectively hydrogenated in a single pot to tetrahydrofurfuryl alcohol (THFAL) over a Si–MFI molecular sieve supported Pd catalyst. Studies on catalyst screening revealed that both the metal function and the support were critical for directing the selectivity to the ring-hydrogenated product, THFAL. The structural feature of MFI as shown by XRD was completely retained in the used sample of the 3% Pd/MFI catalyst confirming its stability under reaction conditions. XRD, along with SEM characterization of the used samples, established retention of morphology of the structured silicate, suggesting a strong interaction between hexagonal porous silicate and Pd particles. The complete conversion of FFR with an enhanced selectivity of 95% to THFAL could be achieved by recycling the crude of the first hydrogenation experiment over the same 3% Pd/MFI catalyst.

KEYWORDS: *Biomass conversion, Hydrogenation, Pd/MFI, THFAL, Recyclability*

■ INTRODUCTION

In the era of continued depletion of fossil resources, extensive research is focused on catalytic conversion of biomass as it forms a basis for sustainable production of energy and chemicals.[1−3] However, biomass-derived molecules contain high oxygen content; hence, novel catalysts for efficient protocols are being investigated for selectively tailoring their oxygen content to achieve the desired product mix.[4−6] In this context, furfural (FFR) is a highly attractive molecule derived from defunctionalization of the most abundantly available lignocellulose for the production of fuels and chemical intermediates.[7−10] FFR is mainly produced by acid hydrolysis of pentose sugars C5 (xylose, arbinose) followed by a loss of three water molecules.[11−15] It is a versatile carbohydrate-derived starting material for mainly aldol condensation and hydrogenation.[16,17] The catalytic hydrogenation of either side-chain carbonyl or ring or both gives a variety of useful products such as furfuryl alcohol (FAL), tetrahydrofurfuryl alcohol (THFAL), 2-methylfuran (2-MF), and 2-methyl tetrahydrofuran (2-MTHF).[18−23] One of these products, THFAL, is an environmentally acceptable "green" industrial solvent due to its biodegradable nature.[24,25] A variety of catalysts including both noble and non-noble metals have been reported for selective vapor as well as liquid phase hydrogenation of FFR. Noble metal catalyst systems reported for vapor phase hydrogenation of FFR under severe temperature and pressure conditions (200−300 °C and 100 bar H_2) yield not only the desired products but also a variety of byproducts including furan, tetrahydrofuran, and even ring-opening products, such as pentanol and pentanediols.[26−28] On the other hand, non-noble catalyst systems, mainly copper chromite, was most often employed in industry for the selective production of FAL from FFR in liquid as well as vapor-phase hydrogenation; however, it poses a serious drawback due to the highly toxic nature of Cr.[29,30]

Although conventionally THFAL is produced by a two-step catalytic hydrogenation of furfural (FFR) via furfuryl alcohol over Cu−Cr and noble metal catalysts separately,[31] direct conversion of FFR to THFAL also has been attempted recently. Sitthisa et al. reported Cu, Pd, and Ni supported on silica, among which only 5% Ni/SiO_2 was found to give THFAL directly at 230 °C with 5% selectivity.[32] Enhanced selectivity of 26% to THFAL could be achieved using a homogeneous Ru(II) bis(diimine) catalyst,[33] while bimetallic transition metal catalysts showed only 4% selectivity to THFAL.[34] Higher THFAL selectivity of 38% was possible over a Raney nickel catalyst at a partial furfural conversion of 50%.[35] Recently, Tomoshige et al. proposed the total hydrogenation of FFR to THFAL in two steps, first step involving FFR conversion to FAL and then in the second step, FAL to THFAL, with 94% yield of THFAL.[20] In all these studies, optimum THFAL selectivity was either possible in a two-step strategy or at partial FFR conversion. There has been hardly any reports on direct conversion of FFR giving appreciable selectivity to THFAL, which could be only possible by structural modification of the catalyst and or the support.

Zeolite, microporous crystalline aluminosilicate, has attracted extensive interest, owing to its uniform micropore size distribution, high thermal and hydrothermal stability, flexible

Received: August 18, 2013
Revised: October 15, 2013
Published: October 28, 2013

framework to tune the surface properties, and high internal surface area. MFI-type zeolite, ZSM-5, is a medium-pore high-silica zeolite with cavities and channels of molecular dimension from 5 to 6 Å. The MFI structure is nonisotropic with sinusoidal pores (diameter ca. 5.5 Å) running in the α-direction and slightly wider straight pores running in the β-direction, and connections between the two pore systems create a three-dimensional network of the pores. Because of the structural architecture, a very high metal dispersion (atomic dispersion) and therefore a very high reaction rate can be achieved for the catalysts containing Pd in the cavities of the MFI framework. Such systems have been studied for important reactions like NO reduction with methane, palladium acetate immobilized in a hierarchical MFI zeolite-supported ionic liquid for the Suzuki reaction in water, etc.[36−38] In view of the moderate catalytic performance of Pd/ZSM-5 and lack of literature on hydrogenation of furfural over Pd/MFI, the research work with relation to investigations on the feasibility of furfural hydrogenation over Pd loaded on all silica MFI-type molecular sieves (Pd/MFI) was undertaken.

Here, we report for the first time, a 3% Pd/MFI catalyst in which MFI was structurally modified by Pd incorporation that resulted in almost complete conversion of FFR (a model compound) with 67−95% selectivity to THFAL in the direct hydrogenation of furfural. The parameter optimization study showed that increased selectivity to THFAL by two times could be achieved with an increase in H_2 pressure and temperature. Reusability of the catalyst was also studied up to five times to confirm the stability of the catalyst under reaction conditions.

EXPERIMENTAL SECTION

Materials. The reagents used for preparation of MFI are tetraethyl ortho silicate (TEOS, 98%, Aldrich), tetra propyl ammonium hydroxide (TPAOH, aq. 20% soln., V. P. Chemical, Pune), furfural (Aldrich), HCl (Thomas Baker), IPA (Thomas Baker), $PdCl_2$ (Aldrich), and distilled water.

Catalyst Preparation. The all silica MFI-type molecular sieve Si−MFI was prepared by following a similar dry gel conversion method described elsewhere[39] using dry gel having a composition of SiO_2:0.23 $(TPA)_2O$.

Supported Pd/MFI catalyst was prepared by the impregnation method. For the preparation of 3% Pd/MFI catalyst, 0.159 g of $PdCl_2$ was dissolved in a minimum amount of dilute hydrochloric acid ensuring the complete dissolution of the precursor. Agitation was done with a magnetic stirring bar. Under stirring, 2 g of slurry of MFI support prepared in water was added to the above solution, and the temperature was maintained at 353 K. After 1 h, 10 molar sodium hydroxide solution was added under stirring to make pH 7−8, and it was stirred for 30 min. After 30 min, 3 mL of formaldehyde was added as a reducing agent under stirring. The solution was cooled and filtered and washed with distilled water to make it Cl^- free, and the solid catalyst obtained was dried at room temperature under vacuum. All other catalysts were prepared using the above method.

Catalyst Characterization. Both BET surface area of all the catalysts and metal dispersion of Pd/MFI and 3% Pd/SiO_2 catalysts were measured using Micromeritics Chemisorb 2720 instrument, by the nitrogen adsorption/desorption (77 K) and chemisorption of 5% H_2 in Ar, respectively. The crystallinity and phase purity of Si−MFI samples were analyzed by powder X-ray diffraction (XRD) patterns using a X-ray diffractometer (Rigaku Miniflex, Japan) with Cu Kα radiation. The N_2 adsorption isotherms were analyzed in a conventional manner, and the pore size distribution was calculated using the DFT method on a Quantachrome QuadraWi version 5.02 instrument. Morphology of MFI and Pd supported on MFI catalysts were examined by scanning electron microscopy (SEM), and the presence of Pd loading was confirmed by EDX analysis on a LEO−LEICA STEREOSCAN 440 instrument. Particle size and morphology were studied using transmission electron microscope (HR-TEM), model JEOL 1200 EX. A small amount of the solid sample was sonicated in 2-propanol for 1 min. A drop of prepared suspension was deposited on a Cu grid coated with a carbon layer, and the grid was then dried at room temperature before analysis. After carrying out the leaching experiment, the supernatant liquid was evaporated and the resulting product concentrate was treated with aqua regia (HNO_3:HCl = 1:3) at 60 °C on a sand bath for 2 h and then made up to 25 mL with distilled water. This sample was then analyzed by an ICP-OES instrument.

Catalyst Activity. Hydrogenation of furfural reactions were carried out in a 300 mL capacity autoclave (Parr Instruments Co., U.S.A.) at an agitation speed of 1000 rpm. The typical hydrogenation conditions were temperature, 493 K; furfural concentration, 5 wt %; solvent, 95 mL; catalyst loading, 0.5 g; and hydrogen pressure, 3−4 MPa. Liquid samples were withdrawn from time to time. Samples taken during the reaction were analyzed with a Trace GC 700 series GC System (Thermo Scientific) coupled with a FID detector and capillary column (HP-5 capillary column, 30 m length × 0.32 mm id). The following temperature program method was used for GC analysis: 40 °C (3 min), 1 °C/min, 45 °C (1 min), 10 °C/min, 60 (0 min), 20 °C/min, and 250 (1 min). Performance of 3% Pd/MFI catalyst was evaluated in terms of (%) conversion of FFR and (%) product selectivity that are defined below.

$$(\%)\ \text{Conversion} = 1 - \frac{\text{amount of furfural molecules recovered}}{\text{amount of furfural molecules introduced}} \times 100 \quad (1)$$

$$(\%)\ \text{Selectivity} = \frac{\text{amount of each product}}{\text{sum of amount of products}} \times 100 \quad (2)$$

$$(\%)\ \text{Recovery} = \frac{\text{sum of amount of product molecules and unreacted furfural molecules}}{\text{amount of furfural molecules introduced}} \times 100 \quad (3)$$

RESULTS AND DISCUSSION

Catalyst Characterization. Among all the catalysts screened for hydrogenation of furfural, Pd on structured silica (MFI) showed the highest conversion and selectivity to the ring-hydrogenated product THFAL; hence, a detailed characterization of this catalyst is discussed below.

Table 1 shows the BET surface area of all the samples screened in this work. The designate showed the highest surface area of 312 m^2/g, while the surface area decreased with loading of various metals (Pd, Ru, and Cu). The lowest surface area of 32 m^2/g was observed for a combination of Pd−Cu in which the Cu loading was as high as 20%. In the case of 3% Pd loading on MFI, the surface area marginally decreased from 312 to 281m^2/g due to the dispersion of palladium over the MFI support. Table 2 shows the metal dispersion of catalysts with varied Pd loadings on MFI and also that of 3% Pd/SiO_2 along with their respective TOF and TON values. The 3% Pd/MFI showed the highest TON and TOF compared to those of 1%, 5% Pd/MFI and 3% Pd/SiO_2. The structured silicalite (MFI) showed marginally

Table 1. BET Surface Area for Various Supported Catalysts

sample no.	catalysts	BET surface area (m^2/g)
1	MFI	312
2	3% Pd/MFI	281
3	3% Ru/MFI	212
4	3% Pd−3% Ru/MFI	271
5	3% Pd−20% Cu/MFI	32

Table 2. Metal Dispersion of Pd Metal Over MFI Support

entry	catalyst	metal dispersion (%)	TON	TOF (h^{-1})
1	1% Pd/MFI	18	915	183.0
2	3% Pd/MFI	28	1192	238.4
3	5% Pd/MFI	32	1122	224.4
4	3% Pd/SiO_2	25	1090	218

higher metal dispersion (28%) than that of fumed silica (25%). Powder X-ray diffraction patterns of MFI, fresh 3% Pd/MFI, and used 3% Pd/MFI catalysts are shown in Figure 1, which exhibit peaks at 2θ = 8.01°, 8.80°, 8.90°, 23.01°, 23.84°, and 24.07° corresponding to the crystalline MFI structure and orthorhombic symmetry.[40] The characteristic XRD peaks for Pd at 2θ = 38° and 46° could not be identified well as these were found to overlap with those of MFI at the same 2θ values. As seen from XRD of the used sample, the structure of MFI remained unchanged even after exposure of the sample to reaction conditions. This was also in good agreement with the HRTEM results discussed later.

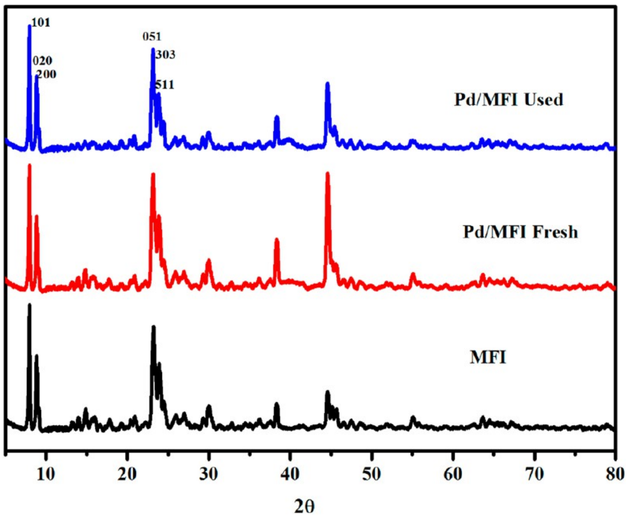


Figure 1. XRD pattern for (A) MFI, (B) 3% Pd/MFI fresh, and (C) 3% Pd/MFI used.

The N_2 adsorption isotherm of structured MFI showed a type-I adsorption isotherm, which was confirmed by the increase in the uptake of nitrogen with characteristic hysteresis (Figure 2a) loops extending from P/Po = 0.2−1. In a detailed study, the nature of the pores was elucidated by adsorption isotherms having a slight phase transition from orthorhombic to monoclinic or a mixture of these two phases. In accordance with the microporosity, the larger pore volume of 0.181 mL/g was observed for MFI (Figure 2b). While a decrease in pore volume to 0.17 mL/g was observed for 3% Pd/MFI (Figure 3a) due to the dispersion of palladium metal particles over MFI.[41,42]

The SEM-EDAX of MFI and Pd/MFI are shown in Figures 4 and 5. A typical intergrown disc-shaped morphology with a hexagonal orientation of MFI having a 0.5−1 μm size was observed. A similar pattern was observed even after loading the Pd metal on MFI. EDAX results confirmed the presence of Pd particles in the structured silicalite with approximately the same loading as taken for the preparation.

HR-TEM results of fresh 3% Pd/MFI and used 3% Pd/MFI are shown in Figure 6. These revealed that the particle size of both the samples was found to be in the range of 150−200 nm, and the silicalite crystals resemble a round disc-shaped morphology in a side view, and planar crystals have a hexagonal shape with a flip structure of MFI matching an orthorhombic symmetry of zeolite phase corresponding with XRD results. While in the case of the 3% Pd/MFI sample, Pd metal particles were seen to be homogeneously dispersed on a silicate sheet of MFI. As shown from the XRD and SEM results even after exposure to the reaction conditions, the morphology of the structured silicate was intact, suggesting a strong interaction between the hexagonal porous silicate and Pd particles.[43]

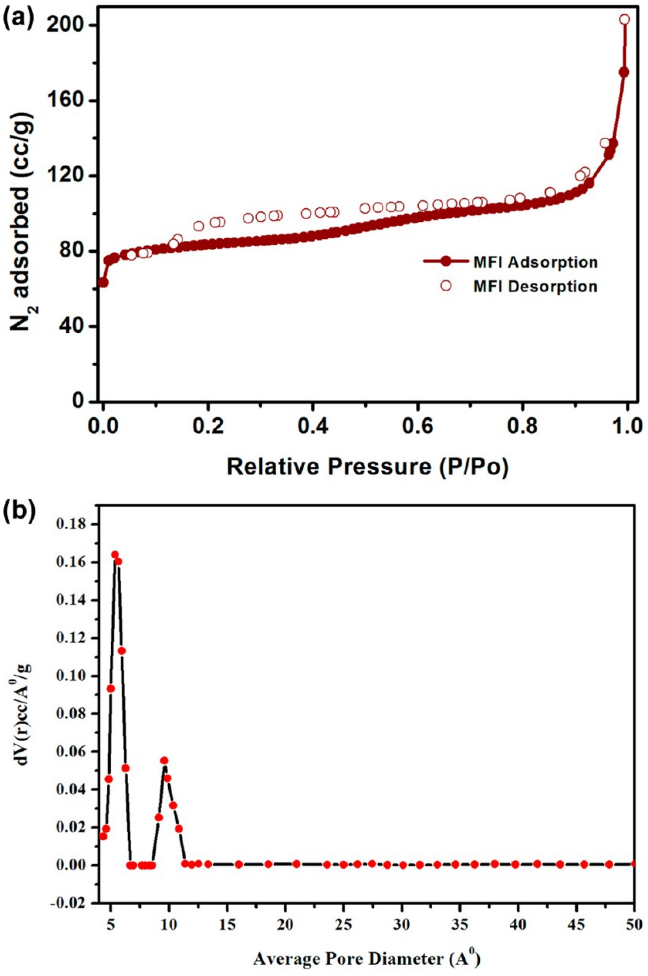


Figure 2. (a) Nitrogen adsorption−desorption isotherm of MFI. (b) Pore size distribution of MFI.

Activity Studies. Several supported metal catalysts were screened for the hydrogenation of furfural, and their activity results are shown in Table 3. On the basis of the dispersion values, TON and TOF calculated for 3% Pd/MFI were also found to be as high as 1192 and 238 h^{-1}, respectively, among all the catalysts (Table 2). As shown in this table, 3% Pd/MFI showed the highest selectivity of 67% to THFAL with 93% conversion of FFR. The unique structural feature of Pd/MFI contributing to the higher selectivity to THFAL was distinctly obvious when the 3% Pd/SiO_2 catalyst showed substantially lower conversion of 76% with a major product as FAL (50%) and only 31% selectivity to THFAL along with 19% of byproduct formation (Table 3, entry 2). Figure 7 shows the % conversion of FFR and % selectivity of FAL and THFAL as a function of reaction time over 3% Pd/MFI. It was observed that both FAL and THFAL were formed in the beginning of the reaction,

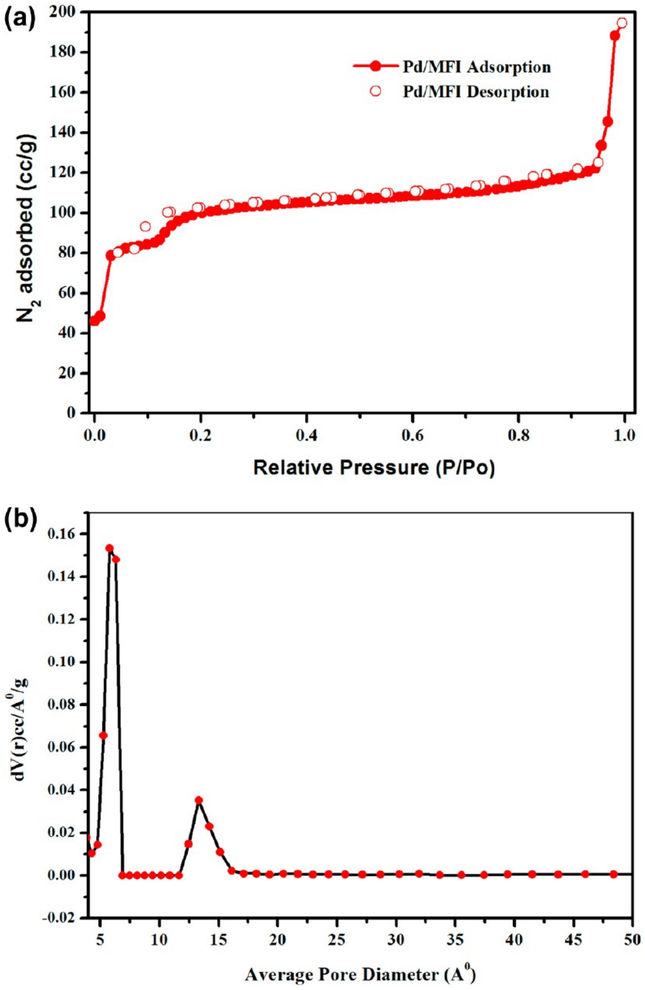


Figure 3. (a) Nitrogen adsorption−desorption isotherm of 3% Pd/MFI. (b) Pore size distribution of 3%Pd/MFI.

although % selectivity of FAL was higher than that of THFAL. As the reaction proceeded beyond 1 h, selectivity to FAL started depleting, while that of THFAL was increasing, which indicates the consecutive hydrogenation of FFR to FAL and then to THFAL. Figure 7 also shows that 3% Pd/MFI gave a conversion of 38% with 46% selectivity to THFAL in 1 h while, 3% Pd/SiO_2 catalyst gave only a 19% conversion with 20% selectivity to THFAL in 1 h (Figure 8), which confirms the efficient role of the MFI support in enhancing the activity and THFAL selectivity.

Because MFI as a support showed optimal activity and THFAL selectivity, it was further modified to impart Lewis acidity by incorporating Sn^{4+} in a MFI framework. However, such a surface modification adversely affected both activity and THFAL selectivity of Pd/MFI. Thus, only the textural property of MFI was the contributing factor for the highest conversion and THFAL selectivity. Further catalyst optimization was attempted by changing Pd to Ru as the latter is known to be effective for ring hydrogenation.[44] Contrary to our expectation, 3% Ru/MFI gave a major product as FAL (79% selectivity), while THFAL was a minor (13% selectivity) product. Although, Ru in combination with Pd resulted in complete FFR conversion, THFAL selectivity enhanced to only 49% (Table 3, entry 5) which was still lower than monometallic 3% Pd/MFI (Table 3, entry 1). Another bimetallic combination of Pd with a non-noble metal such as Cu was also evaluated, which showed a very interesting result of >90% selectivity to FAL and the remaining diacetal product (Table 3, entry 6). The major activity was shown by Cu (20% loading) for the first stage FFR hydrogenation.[45] Both these results demonstrate that only the monometallic 3% Pd/MFI catalyst is efficient for single-step FFR hydrogenation to THFAL, rather than any bimetallic combination. This aspect needs to be further investigated through surface characterization in detail.

The complete conversion of FFR with an enhanced selectivity of 95% to THFAL could be achieved by recycling the crude of the first hydrogenation experiment over the same 3% Pd/MFI (Table 3, entry 7) catalyst. Hence, a continuous hydrogenation over a bed of a 3% Pd/MFI catalyst with an optimized feed flow rate would result in a very high productivity of the process. The reaction pathway to THFAL going through FAL intermediate

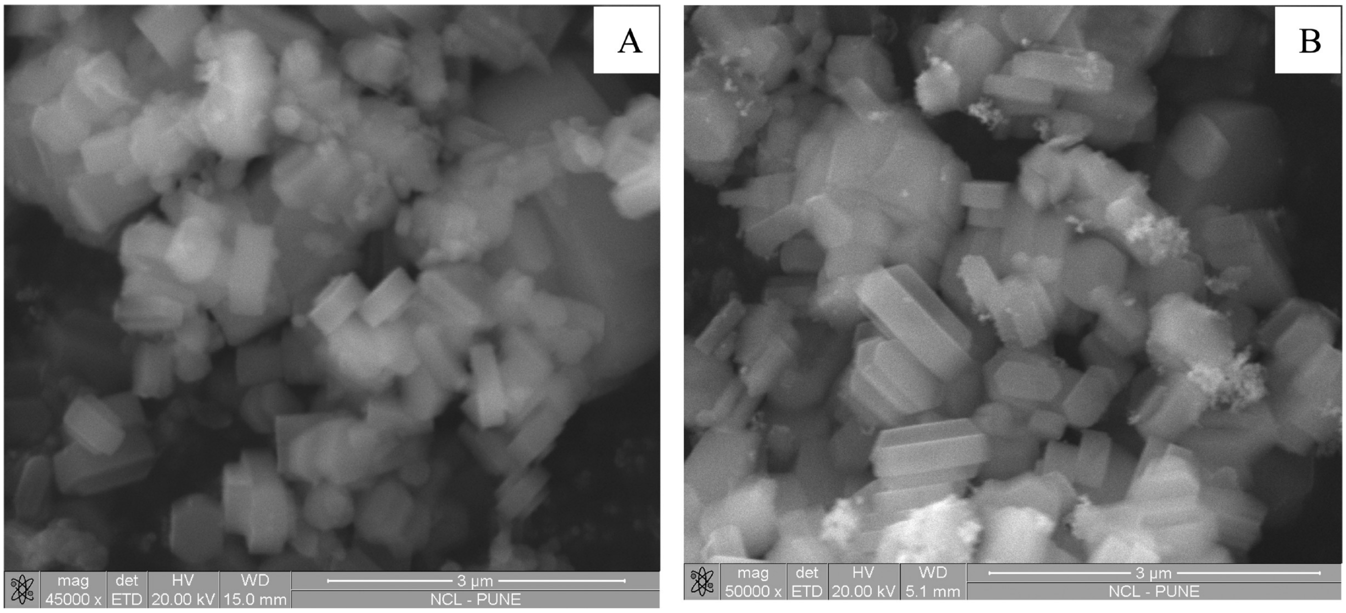
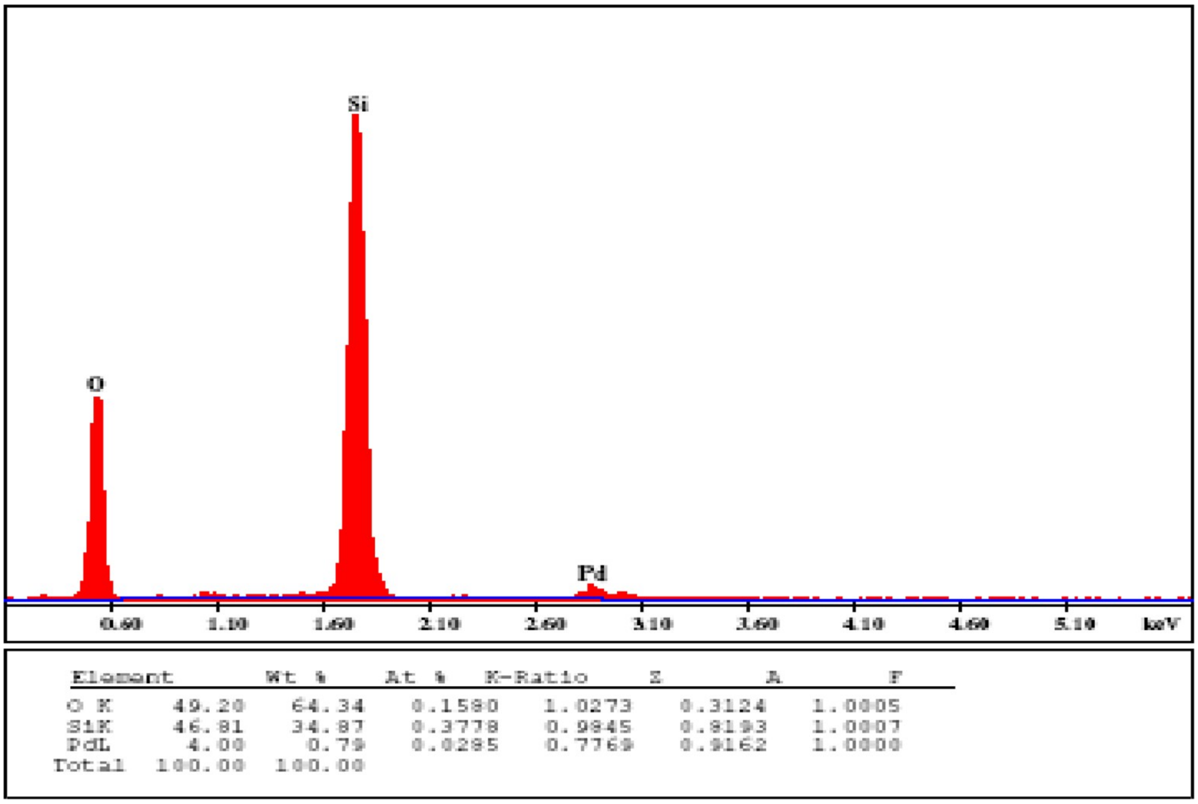


Figure 4. SEM images for (A) 3% Pd/MFI fresh and (B) 3% Pd/MFI used.



Element	Wt %	At %	K-Ratio	Z	A	F
O K	49.20	64.34	0.1580	1.0273	0.3124	1.0005
SiK	46.81	34.87	0.3778	0.9845	0.8193	1.0007
PdL	4.00	0.79	0.0285	0.7769	0.9162	1.0000
Total	100.00	100.00				

Figure 5. EDAX of Pd/MFI.

(Scheme 1) was confirmed by a control experiment in which FAL was used as a substrate. As expected, almost complete selectivity (>95%) to THFAL was achieved in this case (Table 3, entry 8). The 3% Pd/MFI is the most active catalyst for direct hydrogenation of FFR to THFAL because of the strong interaction between the Pd metal and π electrons of the FFR molecule resulting from rehybridization of sp^2 to sp^3 of C on the Pd surface.[32]

Optimization of Reaction Parameters. Figure 9 shows the results of the effect of hydrogen pressure on hydrogenation of furfural (FFR) at 493 K. FFR conversion increased marginally from 70% to 93% as the pressure increased from 250 to 500 psi, and it increased further to 97% as the pressure increased from 500 to 750 psi. However, THFAL selectivity increased substantially from 35% to 67% at 500 psi H_2 pressure. Increase in activity with an increase in hydrogen pressure was obviously due to a greater concentration of surface hydrogen available on the active catalyst site, which facilitates the FFR hydrogenation to THFAL.

Figure 10 shows the effect of reaction temperature on FFR conversion and THFAL selectivity over the 3% Pd/MFI catalyst at 500 psi H_2 pressure. Conversion of FFR increased from 72% to 93% with an increase in reaction temperature from 453 to 493 K. The selectivity to THFAL also increased from 56% to 67%. The effect of FFR concentration in the range of 5−20 wt % on conversion and selectivity is shown in Figure 11. The conversion of FFR dramatically decreased from 93% to 68% as the concentration of FFR increased from 5% to 20 wt %. The decrease in conversion of FFR was due to the limiting number of catalyst active sites at a high FFR concentration. The decrease in conversion at higher concentration (20%) of FFR was also associated with an increase in selectivity to FAL up to 71% at the cost of THFAL selectivity (27%). This also suggests a case of competitive adsorption of the substrate FFR and the intermediate FAL on the active sites of the catalyst.[46]

Figure 12 shows the effect of catalyst concentration on the conversion and selectivity pattern in the range of 0.250−0.750 g at 493 K and 500 psi H_2 pressure. The conversion of FFR increased sharply from 65% to 98% as the catalyst concentration increased by three folds from 0.250 to 0.750 g. The increase in FFR conversion was due to a higher concentration of active sites available for hydrogenation. The selectivity to THFAL also increased marginally from 67% to 73% at higher catalyst concentration.

Figure 13 shows the effect of Pd metal loading over a MFI support. It was observed that when the Pd metal loading was decreased to 1%, the conversion of FFR also decreased to 46% with 78% selectivity to FAL and 22% selectivity to THFAL. The decrease in selectivity was due to the lower Pd metal loading that retarded further hydrogenation of FAL to THFAL. Increase in Pd metal loading to 5% resulted in almost complete conversion of FFR with 28% selectivity to FAL, 49% to THFAL, and 23% selectivity to 1,2 pentanediol. It is very interesting to note that 1,2 pentanediol formation was due to further hydrogenation of THFAL at higher Pd loading.

Catalyst Recycle Study. The 3% Pd/MFI catalyst was recycled for four times, and the results are shown in Figure 14. The catalyst recycle study was carried out as follows. After the first reaction, the reactor was allowed to cool, and the catalyst was allowed to settle down. The supernatant liquid product was removed, and the fresh substrate along with the solvent were charged to the reactor for a subsequent reaction. The same procedure was followed for four times for which almost the same performance as that of the fresh catalyst was observed. The stability of the catalyst was also confirmed by XRD, where the structure of the catalyst was found to remain the same after the

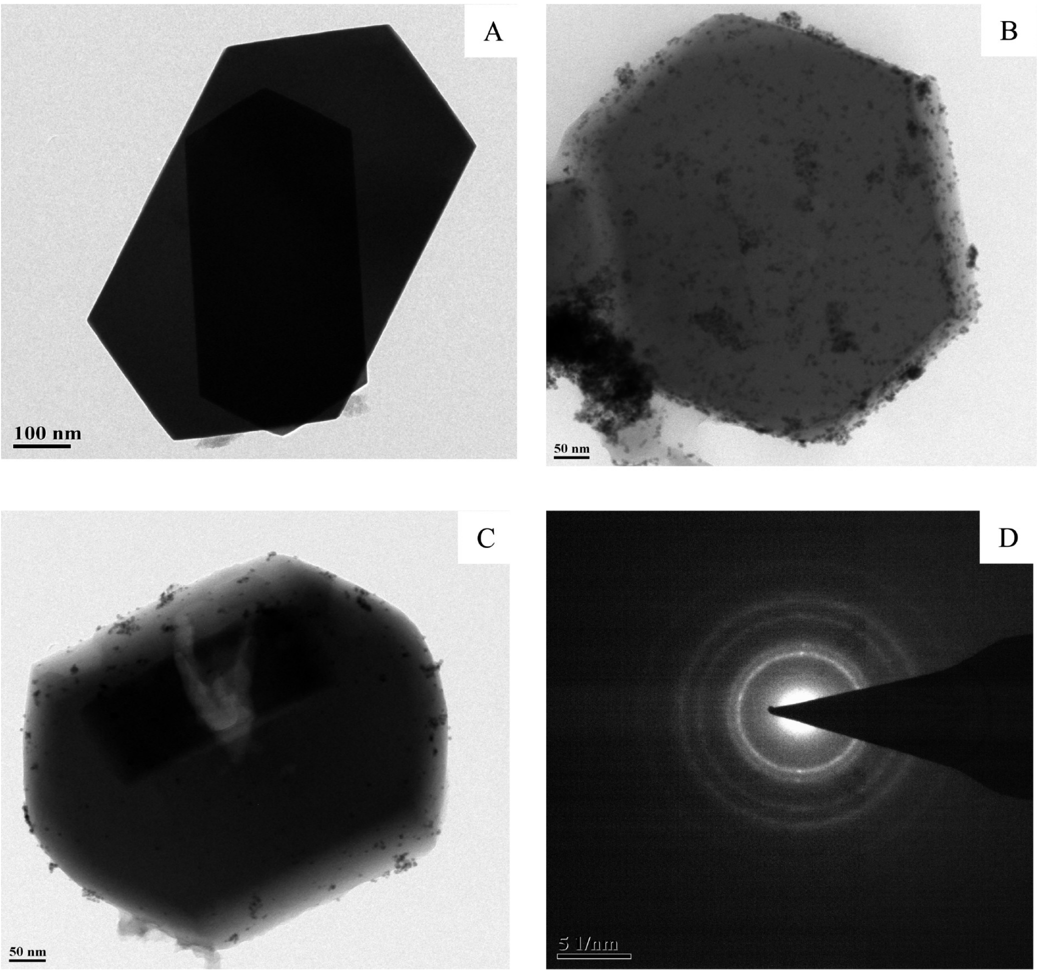


Figure 6. HR-TEM images for (A) MFI, (B) 3% Pd/MFI fresh, and (C) 3% Pd/MFI used. (D) SAD image.

Table 3. Catalyst Screening for Furfural Hydrogenation[a]

			selectivity %							
sample no.	catalyst	conversion %	FAL	THFAL	MF	MTHF	THF	diacetal	hemiacetal	others
1	3% Pd/MFI	93	31	67	–	–	2	–	–	–
2	3% Pd/SiO_2	76	50	31	–	–	–	–	–	19
3	3% Pd/SnMFI	72	49	30	1	–	2	3	9	6
4	3% Ru/MFI	100	79	13	2	–	–	2	1	3
5	3% Pd–3% Ru–MFI	98	29	49	4	1	3	9	–	5
6	3% Pd–20% Cu–MFI	100	91	–	–	–	–	9	–	–
7	3% Pd/MFI[b]	100	3	95	–	–	2	–	–	–
8	3% Pd/MFI	84	SM	99	1	–	–	–	–	–

[a] Reaction conditions: substrate, 5% (W/W); solvent, isopropyl alcohol (95 mL); temperature, 493 K; pressure, 500 psi; agitation speed, 1000 rpm; catalyst (3% Pd/MFI), 0.5 g; and reaction time, 5 h. [b] Reaction conditions: reaction crude; temperature, 493 K; pressure, 500 psi; agitation speed, 1000 rpm; catalyst (3% Pd/MFI), 0.5 g; and reaction time, 5 h.

recycle experiments (Figure 1). There was slight decrease in the conversion of FFR from 93% to 81% at the end of fourth reuse. ICP-OES analysis of the reaction crude did not show the presence of any Pd metal, ruling out the possibility of Pd metal leaching under the reaction conditions, and the loss of activity could be merely due to the physical loss of catalyst during withdrawal of samples from time to time for analysis. In order to confirm this further, a standard leaching test was also carried out in which the hot reaction crude was filtered after partial furfural conversion to remove the catalyst. The reaction was again continued with the filtrate devoid of catalyst, which did not show any conversion (Figure 15).

■ CONCLUSION

Among several monometallic as well as bimetallic Pd, Ru, and Cu catalysts on various supports, 3% Pd/MFI showed the highest conversion and THFAL selectivity in the range of 93–100% and 67–95%, respectively, for the direct hydrogenation of furfural in a single reactor. Under optimized conditions, the intermediate furfuryl alcohol formed to the extent that only ~30%, could be completely converted to THFAL by recycling the reaction crude

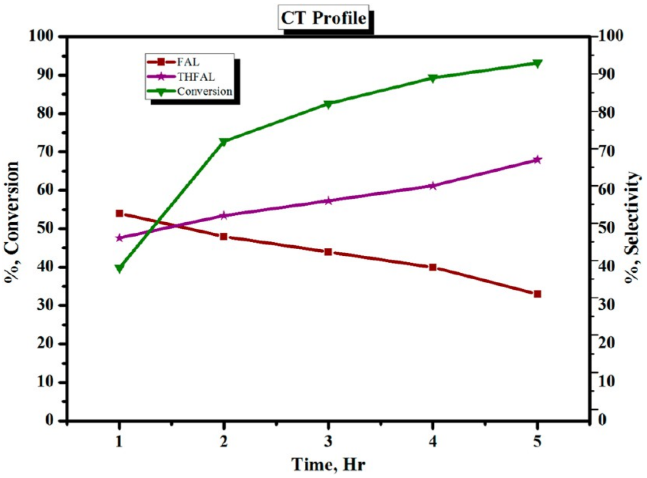


Figure 7. CT profile of hydrogenation of furfural over 3% Pd/MFI catalyst. Reaction conditions: substrate, 5% (W/W); solvent, isopropyl alcohol (95 mL); temperature, 493 K; pressure, 500 psi; agitation speed, 1000 rpm; catalyst (3% Pd/MFI), 0.5 g; and reaction time, 5 h.

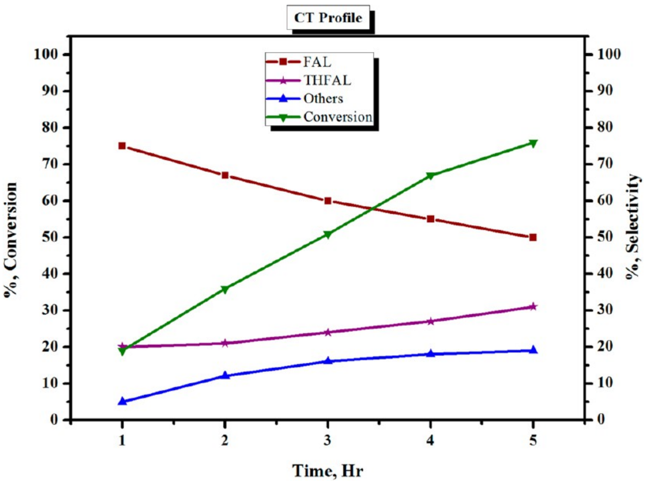


Figure 8. CT profile of hydrogenation of furfural over 3% Pd/SiO_2 catalyst. Reaction conditions: substrate, 5% (W/W); solvent, isopropyl alcohol (95 mL); temperature, 493 K; pressure, 500 psi; agitation speed, 1000 rpm; catalyst (3% Pd/SiO_2), 0.5 g; and reaction time, 5 h.

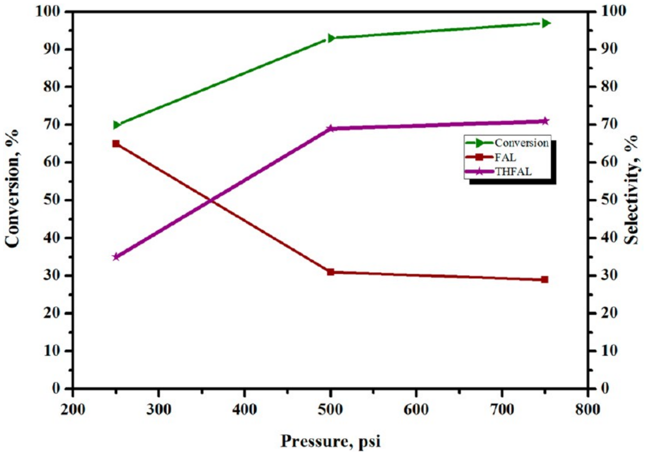


Figure 9. Effect of hydrogen pressure. Reaction conditions: substrate, 5% (W/W); solvent, isopropyl alcohol (95 mL); temperature, 493 K; agitation speed, 1000 rpm; catalyst (3% Pd/MFI), 0.5 g; and reaction time, 5 h.

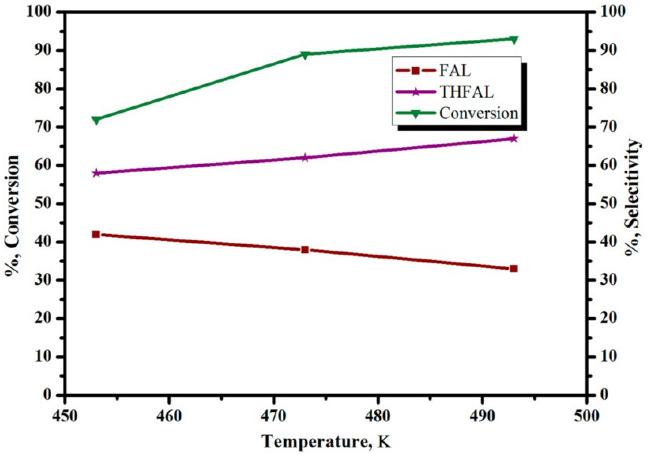
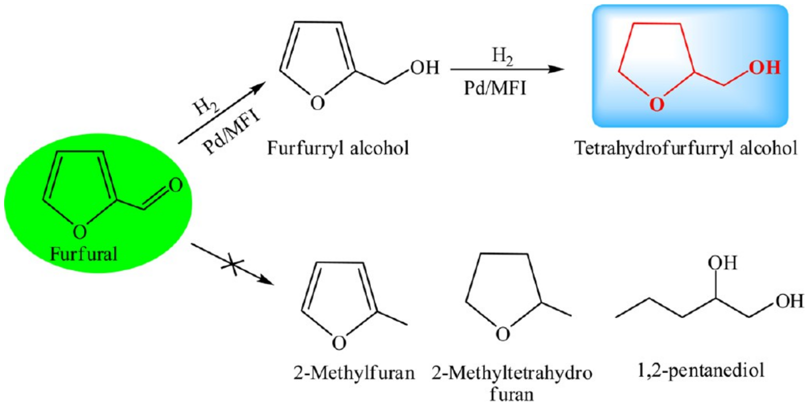


Figure 10. Effect of temperature. Reaction cConditions: substrate, 5% (W/W); solvent, isopropyl alcohol (95 mL); pressure, 500 psi; agitation speed, 1000 rpm; catalyst (3% Pd/MFI), 0.5 g; and reaction time, 5 h.

of the first run. The excellent activity and selectivity of our 3% Pd/MFI catalyst was possible due to structural characteristics of MFI. The initial mesoporous nature of structured MFI was transformed to microporous after impregnation of Pd. The particle size of fresh as well as used catalyst samples was in the range of 150−200 nm as determined by HRTEM, and the silicalite crystals of MFI were hexagonal in shape with a flip

Scheme 1. Hydrogenation of Furfural to Tetrahydrofurfuryl Alcohol



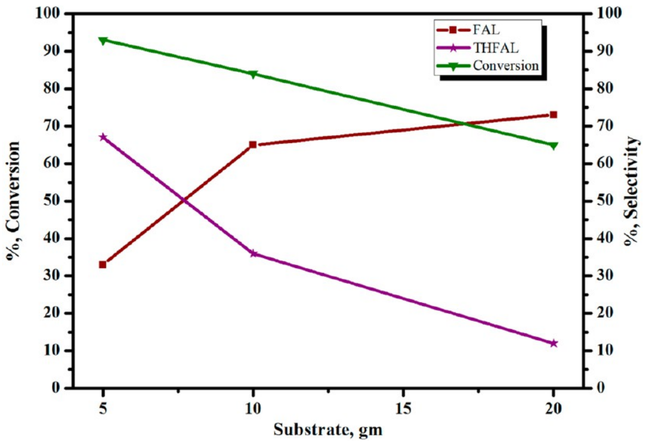


Figure 11. Effect of substrate loading. Reaction conditions: solvent, isopropyl alcohol (95 mL); temperature, 493 K; pressure, 500 psi; agitation speed, 1000 rpm; catalyst (3% Pd/MFI), 0.5 g; and reaction time, 5 h.

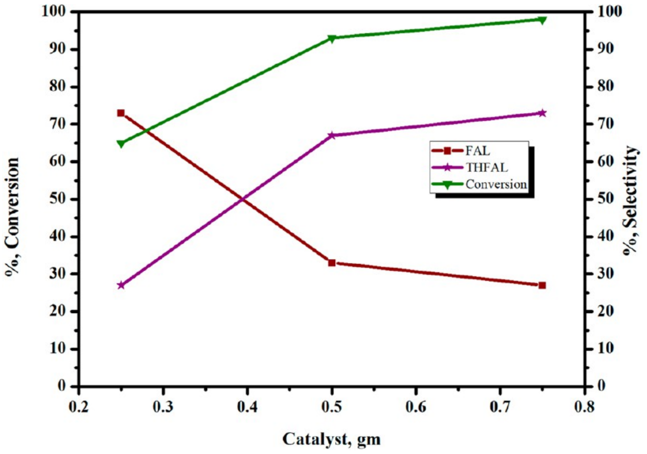


Figure 12. Effect of catalyst loading. Reaction conditions: substrate, 5% (W/W); solvent, isopropyl alcohol (95 mL); temperature, 493 K; pressure, 500 psi; agitation speed, 1000 rpm; and reaction time, 5 h.

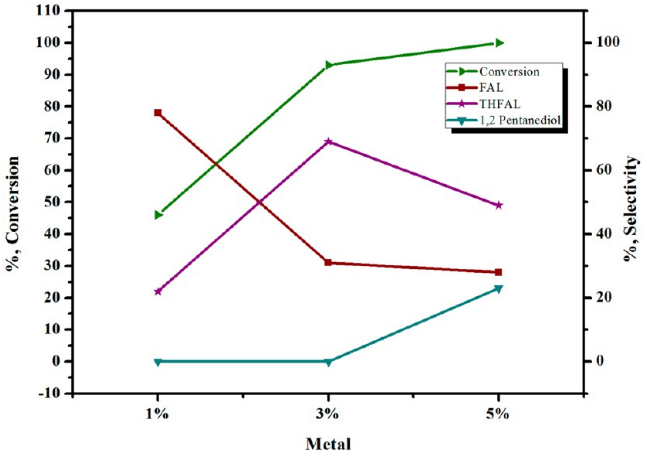


Figure 13. Effect of Pd metal loading. Reaction conditions: substrate, 5% (W/W); solvent, isopropyl alcohol (95 mL); temperature, 493 K; pressure, 500 psi; agitation speed, 1000 rpm; catalyst, 0.5 g; and reaction time, 5 h.

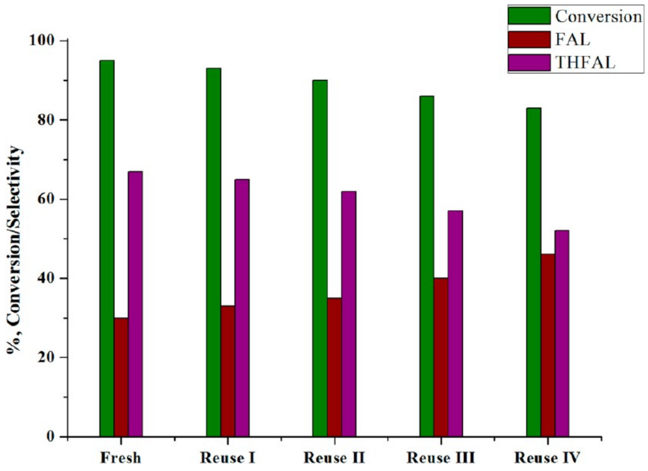


Figure 14. Catalyst recycle study. Reaction conditions: substrate, 5% (W/W); solvent, isopropyl alcohol (95 mL); temperature, 493 K; pressure, 500 psi; agitation speed, 1000 rpm; catalyst (3% Pd/MFI), 0.5 g; and reaction time, 5 h.

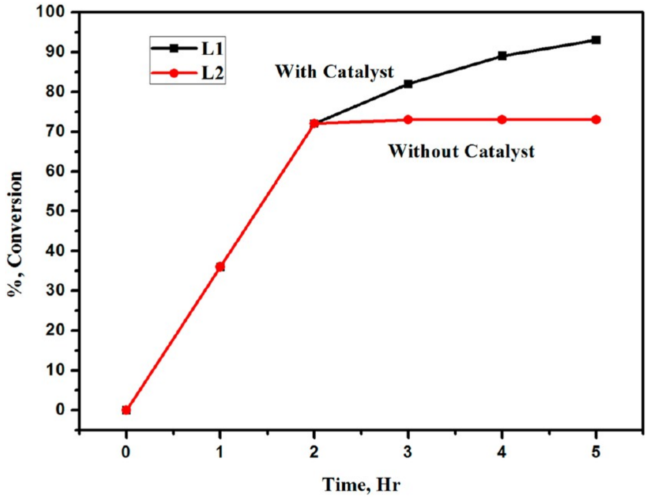


Figure 15. Leaching test. Reaction conditions: substrate, 5% (W/W); solvent, isopropyl alcohol (95 mL); temperature, 493 K; pressure, 500 psi; agitation speed, 1000 rpm; catalyst (3% Pd/MFI), 0.5 g; and reaction time, 5 h.

structure matching an orthorhombic symmetry of zeolite phase corresponding with the XRD results. The catalyst stability was proved by the XRD of the used catalyst as well as its consistent performance up to four recycles.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: cv.rode@ncl.res.in. Tel: 020-5902395.

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 for this work under NMITLI program (TLP 002926).

■ ABBREVIATIONS

FFR: furfural
FAL: furfuryl alcohol
THFAL: tetrahydrofurfuryl alcohol

REFERENCES

(1) Huber, G. W.; Iborra, S.; Corma, A. Synthesis of transportation fuels from biomass: Chemistry, catalysts, and engineering. *Chem. Rev.* **2006**, *106*, 4044−4098.

(2) Corma, A.; Iborra, S.; Velty, A. Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* **2007**, *107*, 2411−2502.

(3) Gallezot, P. Conversion of biomass to selected chemical products. *Chem. Soc. Rev.* **2012**, *41*, 1538−1558.

(4) Bozell, J. J.; Petersen, G. R. Technology development for the production of biobased products from biorefinery carbohydrates—the U.S. Department of Energy's "Top 10" revisited. *Green Chem.* **2010**, *12*, 539−554.

(5) Alonso, D. M.; Wettstein, S. G.; Dumesic, J. A. Bimetallic catalysts for upgrading of biomass to fuels and chemicals. *Chem. Soc. Rev.* **2012**, *41*, 8075−8098.

(6) Egeblad, K.; Hansen, J. R.; Marsden, C. C.; Taarning, E.; Christensen, C. H. Heterogeneous catalysis for production of value-added chemicals from biomass. *Catalysis* **2009**, *21*, 13−50.

(7) Tao, F.; Song, H.; Chou, L. Efficient conversion of cellulose into furans catalyzed by metal ions in ionic liquids. *J. Mol. Catal. A: Chemical* **2012**, *357*, 11−18.

(8) Dutta, S.; De, S.; Saha, B.; Alam, Md.-I. Advances in conversion of hemicellulosic biomass to furfural and upgrading to biofuels. *Catal. Sci. Technol.* **2012**, *2*, 2025−2036.

(9) Karinen, R.; Vilonenm, K.; Niemel, M. Biorefining: Heterogeneously catalyzed reactions of carbohydrates for the production of furfural and hydroxymethylfurfural. *ChemSusChem* **2011**, *4*, 1002−1016.

(10) Daengprasert, W.; Boonnoun, P.; Laosiripojana, N.; Goto, M.; Shotipruk, A. Application of sulfonated carbon-based catalyst for solvothermal conversion of cassava waste to hydroxymethylfurfural and furfural. *Ind. Eng. Chem. Res.* **2011**, *50*, 7903−7910.

(11) Weingarten, R.; Cho, J.; Conner, W. C.; Huber, G. W., Jr. Kinetics of furfural production by dehydration of xylose in a biphasic reactor with microwave heating. *Green Chem.* **2010**, *12*, 1423−1429.

(12) Lam, E.; Majid, E.; Leung, A. C. W.; Chong, J. H.; Mahmoud, K. A.; Luong, J. H. T. Synthesis of furfural from xylose by heterogeneous and reusable nafion catalysts. *ChemSusChem* **2011**, *4*, 535−541.

(13) Chheda, J. N.; Leshkov, Y. R.; Dumesic, J. A. Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides. *Green Chem.* **2007**, *9*, 342−350.

(14) Marcotullio, G.; Jong, W. D. Chloride ions enhance furfural formation from D-xylose in dilute aqueous acidic solutions. *Green Chem.* **2010**, *12*, 1739−1746.

(15) Mao, L.; Zhang, L.; Gao, N.; Li, A. Seawater-based furfural production via corncob hydrolysis catalyzed by $FeCl_3$ in acetic acid steam. *Green Chem.* **2013**, *15*, 727−737.

(16) Vorotnikov, V.; Mpourmpakis, G.; Vlachos, D. G. DFT study of furfural conversion to furan, furfuryl alcohol, and 2-methylfuran on Pd(111). *ACS Catal.* **2012**, *2*, 2496−2504.

(17) Bechem, B.; Patman, R. L.; Hashmi, A. S. K.; Krische, M. J. Enantioselective carbonyl allylation, crotylation, and tert-prenylation of furan methanols and furfurals via iridium-catalyzed transfer hydrogenation. *J. Org. Chem.* **2010**, *75*, 1795−1798.

(18) Baker, L. R.; Kennedy, G.; Spronsen, M. V.; Hervier, A.; Cai, X.; Chen, S.; Wang, L. W.; Omorjai, G. A. Furfuraldehyde hydrogenation on titanium oxide-supported platinum nanoparticles studied by sum frequency generation vibrational spectroscopy: Acid−base catalysis explains the molecular origin of strong metal−support interactions. *J. Am. Chem. Soc.* **2012**, *134*, 14208−14216.

(19) Rodiansono, S. K.; Hara, T.; Ichikunia, N.; Shimazu, S. Highly efficient and selective hydrogenation of unsaturated carbonyl compounds using Ni−Sn alloy catalysts. *Catal. Sci. Technol.* **2012**, *2*, 2139−2145.

(20) Nakagawa, Y.; Nakazawa, H.; Watanabe, H.; Tomishige, K. Total hydrogenation of furfural over a silica-supported nickel catalyst prepared by the reduction of a nickel nitrate precursor. *ChemCatChem* **2012**, *4*, 1791−1797.

(21) Zheng, H. Y.; Zhua, Y. L.; Teng, B. T.; Bai, Z. Q.; Zhang, C. H.; Xiang, H. W.; Li, Y. W. Towards understanding the reaction pathway in vapour phase hydrogenation of furfural to 2-methylfuran. *J. Mol. Catal. A: Chem.* **2006**, *246*, 18−23.

(22) Lessard, J.; Morin, J. F.; Wehrung, J. F.; Magnin, D. High yield conversion of residual pentoses into furfural via zeolite catalysis and catalytic hydrogenation of furfural to 2-methylfuran. *Top. Catal.* **2010**, *53*, 1231−1234.

(23) Zheng, H. Y.; Zhu, Y. L.; Bai, Z. Q.; Huang, L.; Xianga, H. W.; Lia, Y. W. An environmentally benign process for the efficient synthesis of cyclohexanone and 2-methylfuran. *Green Chem.* **2006**, *8*, 107−109.

(24) Yun, S.; Wei, L.; Minghui, Z.; Keyi, T. Hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol on NiB/SiO2 amorphous alloy catalyst. Front. *Chem. Eng. China* **2007**, *1* (2), 151−154.

(25) Tike, M. A.; Mahajani, V. V. Kinetics of liquid-phase hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol over a Ru/TiO_2 catalyst. *Ind. Eng. Chem. Res.* **2007**, *46*, 3275−3282.

(26) Sangeetha, P.; Nagaraja, B. M.; Shanthi, K.; Rama Rao, K. S.; Narayanan, S. Vapour phase hydrogenation of furfural over palladium supported catalysts. *Bull. Catal. Soc. India* **2009**, *8*, 52−63.

(27) Pushkarev, V. V.; Musselwhite, N.; An, K.; Alayoglu, S.; Somorjai, G, A. High structure sensitivity of vapor-phase furfural decarbonylation/hydrogenation reaction network as a function of size and shape of Pt nanoparticles. *Nano Lett.* **2012**, *12*, 5196−5201.

(28) Hronec, M.; Fulajtarova, K. Selective transformation of furfural to cyclopentanone. *Catal. Commun.* **2012**, *24*, 100−104.

(29) Nagaraja, B. M.; Padmasri, A. H.; Seetharamulu, P.; Reddy, K. H. P.; Raju, B. D.; Rama Rao, K. S. A highly active $Cu-MgO-Cr_2O_3$ catalyst for simultaneous synthesis of furfuryl alcohol and cyclohexanone by a novel coupling route: Combination of furfural hydrogenation and cyclohexanol dehydrogenation. *J. Mol. Catal. A: Chem.* **2007**, *278*, 29−37.

(30) Rama Rao, K. S.; Burri, D. R.; Sanakarasubbier, N.; Bhari, M. N.; Aytam, H. P.; Vasireddy, S.; Veldurthi, S.; Podila, S.; Reddy, S. S. Vapour Phase Catalytic Process for Simultaneous Furfural Hydrogenation and Cyclohexanol Dehydration. U.S. 7015359 B1, 2006.

(31) Stevens, J. G.; Bourne, R. A.; Twigg, M. V.; Poliakoff, M. Real-time product switching using a twin catalyst system for the hydrogenation of furfural in supercritical CO_2. *Angew. Chem., Int. Ed.* **2010**, *49*, 8856−8859.

(32) Sitthisa, S.; Resasco, D. E. Hydrodeoxygenation of furfural over supported metal catalysts: A comparative study of Cu, Pd and Ni. *Catal. Lett.* **2011**, *141*, 784−791.

(33) Gowda, A. S.; Parkin, S.; Ladipo, F. T. Hydrogenation and hydrogenolysis of furfural and furfuryl alcohol catalyzed by ruthenium(II) bis(diimine) complexes. *Appl. Organometal. Chem.* **2012**, *26*, 86−93.

(34) Vetere, V.; Merlo, A. B.; Ruggera, J. F.; Casella, M. L. Transition metal-based bimetallic catalysts for the chemoselective hydrogenation of furfuraldehyde. *J. Braz. Chem. Soc.* **2010**, *21* (5), 914−920.

(35) Lee, S.-P.; Chen, Y. W. Selective hydrogenation of furfural on Ni−P, Ni−B, and Ni−P−B ultrafine materials. *Ind. Eng. Chem. Res.* **1999**, *38*, 2548−2556.

(36) Adelmana, B. J.; Sachtler, W. M. H. The effect of zeolitic protons on NOx reduction over Pd/ZSM-5 catalysts. *App. Catal. B: Environ.* **1997**, *14*, 1−11.

(37) Chen, H. Y.; Wang, X.; Sachtler, W. M. H. Reduction of NOx over zeolite MFI supported iron catalysts: Nature of active sites. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3083−3090.

(38) Jin, M. J.; Taher, A.; Kang, H. J.; Choi, M.; Ryoo, R. Palladium acetate immobilized in a hierarchical MFI zeolite-supported ionic liquid: A highly active and recyclable catalyst for Suzuki reaction in water. *Green Chem.* **2009**, *11*, 309−313.

(39) Niphadkar, P. S.; Kotwal, M. S.; Deshpande, S. S.; Bokade, V. V.; Joshi, P. N. Tin-silicalite-1: Synthesis by dry gel conversion, characterization and catalytic performance in phenol hydroxylation reaction. *Mater. Chem. Phys.* **2009**, *114*, 344−349.

(40) Treacy, M. M. J.; Higgins, J. B. Collection of Simulated XRD Powder Patterns for Zeolites, 4th ed.; Elsevier: Amsterdam, 2001.

(41) Jinka, K. M.; Bajaj, H. C.; Jasra, R. V.; Prasetyanto, E. A.; Park, S. E. Microwave synthesized mesoporous vanadium-mfi catalysts for epoxidation of styrene using molecular oxygen. *Top. Catal.* **2010**, *53*, 238−246.

(42) Shetti, V. N.; Kim, J.; Srivastava, R.; Choi, M.; Ryoo, R. Assessment of the mesopore wall catalytic activities of MFI zeolite with mesoporous/microporous hierarchical structures. *J. Catal.* **2008**, *254*, 296−303.

(43) Philippaerts, A.; Paulussen, S.; Turner, S.; Lebedev, O. I.; Tendeloo, G. V.; Poelman, H.; Bulut, M.; Clippel, F. D.; Smeets, P.; Sels, B.; Jacobs, P. Selectivity in sorption and hydrogenation of methyl oleate and elaidate on MFI zeolites. *J. Catal.* **2010**, *270*, 172−184.

(44) Khan, F. A.; Vallat, A.; Fink, G. S. Highly selective low-temperature hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol catalysed by hectorite-supported ruthenium nanoparticles. *Catal. Commun.* **2011**, *12*, 1428−1431.

(45) Villaverde, M. M.; Bertero, N. M.; Garetto, T. F.; Marchi, A. J. Selective liquid-phase hydrogenation of furfural to furfuryl alcohol over Cu-based catalysts. *Catal. Today* **2013**, *213*, 87−92.

(46) Nadgeri, J. M.; Telkar, M. M.; Rode, C. V. Hydrogenation activity and selectivity behavior of supported palladium nanoparticles. *Catal. Commun.* **2008**, *9*, 441−446.