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Efficient hydrogenation of concentrated aqueous furfural solutions in to furfuryl alcohol under ambient conditions in presence of PtCo bimetallic catalyst

M. G. Dohade,[a] P. L. Dhepe[a,*]

One of the biomass derived significant chemical furfural (FAL) can be hydrogenated to yield industrially important platform chemical, furfuryl alcohol (FOL). Although heterogeneous catalysts based methods are known to yield FOL from dilute solutions of FAL, those mainly operate at higher temperatures and/or high pressures of hydrogen and in presence of organic solvents. In this work, we employ bimetallic PtCo/C catalysts with varying metal concentrations to achieve maximum possible FOL yield (100%) at 35 °C under 0.1 MPa H_2 in water. With concentrated FAL (40 *wt%*) at 50 °C and under 1 MPa H_2 pressure, 86% yield for FOL was observed. Moreover, efficient recycling of catalyst in at least 4 runs with marginal loss in activity due to handling error and isolation of FOL in pure form confirmed by NMR and HPLC is attractive. The characterization of catalysts with several physico-chemical techniques (XRD, TEM, XPS, ICP, TPR) reveal the presence of electron rich Pt and ionic Co species in proximity with each other and those work synergistically to facilitate accomplishment of maximum possible yield of FOL under ambient conditions and in water medium.

Introduction

To circumvent the drawbacks such as, diminishing reserves, fluctuating prices and climate change linked with the use of fossil feedstock; exploitation of non-edible renewable feedstock,[1] lignocellulosics consisting of cellulose, hemicelluloses and lignin to produce chemicals is imperative.[2] Typically, C5 and C6 based polysaccharide, hemicellulose is known to produce furfural (FAL) with high yields through in-series acid catalyzed hydrolysis (to produce C5 sugars) and dehydration reactions.[3-5] Further, furfural can be converted into several industrially important chemicals[6-8] such as furfuryl alcohol (FOL, hydrogenation of -CHO to $–CH_2OH$) and tetrahydrofurfuryl alcohol (THFA, ring hydrogenation and hydrogenation of -CHO to $–CH_2OH$). Next, hydrodeoxygenation (HDO) of FOL produces 2-methylfuran (MF) which has a potential to be used as fuel additive.[6, 9] Besides synthesis of these chemicals, production of methyltetrahydrofuran, γ-valerolactone or valeric acid, ethylfurfuryl and ethyltetrahydrofurfuryl ethers, hydrogenated cyclo products (cyclopentanol, cyclopentanone) as well as various C_{10}–C_{15} coupling products can also be derived from FAL and FOL.[6] It is estimated that ca. 60% of global production of FAL is converted in to FOL.[10] Moreover, this produced FOL acts as a precursor in the preparation of resins, which accounts for more than 85% of total world FOL production.[11, 12]

In view of the significance of FOL, hydrogenation of FAL in to FOL is carried out in presence of various organic solvents like ethanol, methanol, iso-prapanol (IPA) etc. On industrial scale hydrogenation of FAL is performed over Cu-Cr catalyst ($CuCr_2O_4$) at 180 °C under 7-10 MPa of hydrogen pressure in a batch process.[8, 13-22] But owing to employment of high pressures (>7 MPa), toxicity of catalyst (Cr) and deactivation of catalyst (coke formation, sintering, leaching) in the commercial process, impelled researchers to develop Cr free catalytic system for the production of FOL from FAL.[15, 23] Considering this, researchers have studied various other Cu based catalysts (Cu/Al_2O_3, $Cu\text{-}Mg/Al_2O_3$) to produce FOL under lower hydrogen pressures (2 MPa) or in presence of proton donating solvent with mixed success in achieving high yields for FOL (81-100%) with stable catalyst.[12, 24] Besides Cu based catalysts, application of Co-Mo-B alloy (99% FOL yield),[25] 10 *wt%* Co/SBA-15 (88% FOL yield)[26] and polymer stabilized NiB catalysts (71% FOL yield)[27] are too reported to achieve high selectivity (>90%) for FOL formation at 1-2 MPa hydrogen pressures and at 100-180 °C. Recently, conversion of FAL on 2

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* *Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008, India. Tel. 91-20-25902024, E-mail: pl.dhepe@ncl.res.in (P. L. Dhepe)*

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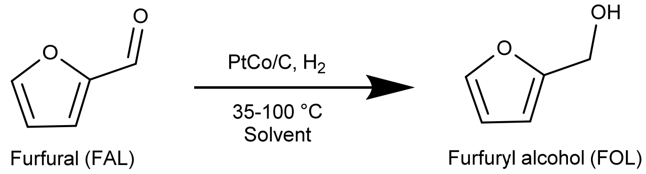
wt% Pt/Al_2O_3 is reported for achieving good selectivity (99%) for FOL under mild conditions in presence of methanol as a solvent.[28] In another report use of 10 *wt%* Pt with same support under 2 MPa hydrogen pressure is shown to hydrogenate FAL to achieve 62% FOL yield.[29] A prevalent observation with Pt catalysts is that due to its very high activity and in the aspiration to accomplish complete conversions, Pt catalysts are prone to catalyze side reactions (hydrogenolysis, hydrogenation, decarbonylation, ring opening etc.) of FAL and FOL, thus lowering the yield for FOL. To suppress these side reactions, Pt only catalysts (46% FOL yield) were decorated with additives such as Sn (96% FOL yield) and Ge (74% FOL yield) and improvement in yields was seen at 100 °C under 1 MPa H_2 pressure with iso-prapanol (IPA) as solvent.[30, 31] Moreover, role of other additives such as, Cu, Fe, heteropolyacid etc. along with other active transition metals (Ni, Ru, Pd etc.) to enhance the yields of FOL is also studied.[8, 10, 25, 32-40] Although with few catalytic systems high yields of FOL are achieved but, recyclability of catalysts, use of dilute substrate solutions and employment of high hydrogen pressures (2-10 MPa) and temperatures (>100 °C) still remains a challenge.[13, 24-26, 29, 41-43] To surmount the use of molecular hydrogen, catalytic transfer hydrogenation of FAL is also performed using IPA and other alcohols as (proton donating) solvents.[24, 44-46] However, mainly these reactions were carried out at higher temperatures (>150 °C) so as to activate the solvent for donation of the proton.[46]

Nevertheless, it would be desirable to use water as a solvent and it is shown that Pd-Cu/MgO catalyzed reactions can be carried out with molecular hydrogen (0.6 MPa; 98% FOL yield)[47-49] or along with inorganic acid like H_3PO_4 (85%) (3 MPa; 27% FOL yield) in presence of water.[50] In yet another report, Ir–ReO_x/SiO_2 catalyst is shown to convert FAL into FOL under milder conditions.[51] But, it is revealed that FAL in water undergoes quite a few side reactions such as rearrangement etc. to produce undesired products and hence the lower yields for FOL are seen.[50, 52] Additionally, leaching and sintering of metals is another key obstacle in employing these catalysts in water medium.

In view of this, it is still a challenge to design a water stable catalyst for the complete conversion of FAL to yield FOL with high selectivity. The addition of secondary metal to stabilize primary (active) metal is helpful in this regard but appropriate choice of these metals is indispensable to attain desired products with high yields as is known from earlier works.[8, 10, 25, 30, 32-40, 43, 53] Considering the limited literature available on water based FAL hydrogenation in achieving higher yields of FOL over stable catalysts, it is requisite to develop an atom efficient water based stable catalytic system to accomplish complete and selective conversion of FAL to FOL under mild reaction conditions (preferably < 50 °C, < 1 MPa H_2) with lower loading of precious metal (Scheme 1). Moreover, to make an overall method industrially attractive it is essential to employ concentrated substrate solutions and hence in this work, reactions are carried out with 40 *wt%* FAL. Based on the earlier studies on acetaldehyde hydrogenation[54] and reduction of the carbonyl group in cinnamaldehyde[55, 56] it was hypothesized that Pt, which activates hydrogen at lower temperatures and oxophilic Co that polarizes carbonyl bond can be combined to achieve higher yields of FOL under milder reaction conditions.



Scheme 1. Conversion of furfural (FAL) to furfuryl alcohol (FOL).

Results and Discussion

Catalyst characterization

The synthesized catalysts were analyzed using ICP-OES technique to quantify the metal contents and the results (Table S1, ESI) explain that the theoretical and experimental values of metal loading are complement with each other very well.

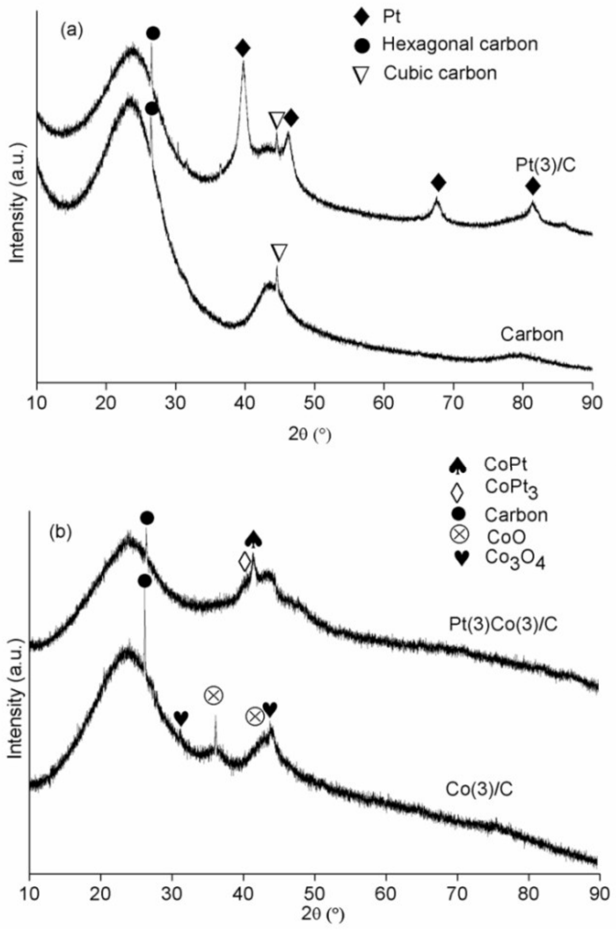


Figure 1. XRD patterns of mono and bimetallic catalysts. (a) Pt(3)/C and reduced carbon; (b) Pt(3)Co(3)/C and Co(3)/C.

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The XRD patterns for mono and bimetallic reduced catalyst samples of Pt and Co supported on carbon are presented in Figure 1. The XRD pattern for Pt(3)/C shows diffraction peaks at 2θ of 39°, 46°, 67° and 81°, which are attributed to the Pt (111), (200), (220) and (311) crystalline planes, respectively of face-centered cubic (fcc) structure of Pt with a space group Fm-3m (JCPDS File No. 01-088-2343).[57] The diffraction peaks at 2θ of 31.47°, 44.24° in Co(3)/C sample indicates the presence of Co in the form of face-centered cubic Co_3O_4 with a space group Fd-3m (JCPDS File No. 09-0418) and peaks at 36.58°, 42.43° specify the occurrence of cubic CoO species with space group Fm-3m (JCPDS File No. 09-0402).[58] From XRD results, it is suggested that Co is present in the mixed oxide form namely, CoO and Co_3O_4 with Co in (II) and (III) oxidation states. In case of diffraction pattern of bimetallic catalyst, Pt(3)Co(3)/C, absence of peak for Pt(111) and appearance of new peak at 41.60° discloses the formation of alloy[59] with foremost contribution from tetragonal CoPt species with a space group P4/mmm (JCPDS File No. 29-0498). A weak peak in this sample at 40.5° is attributed to the formation of trace quantity of cubic $CoPt_3$ species with a space group Pm-3m (JCPDS File No. 29-0499). The non-appearance of peak(s) for any of the Co oxide species in bimetallic Pt(3)Co(3)/C catalyst is because mostly Co is located in the proximity of Pt and is engaged in the formation of alloy.[59] It is also postulated that due to overall low intensity of peaks and overlapping of many peaks in the same 2θ range, it is probable that many of the peaks are masked. Additionally, it is feasible that Co might be present in the amorphous form and thus is not detected. Literature also claims that in a $CoPt_3$ alloy system with an increase in temperature (>500 °C) under reducing condition, sufficient energy to reduce Co is received.[60] In this work, catalysts are reduced at 400 °C and thus it is possible that Co is present in ionic form. Thus, from XRD analysis it is suggested that Pt may assist reduce Co to form Co(0) species unlike in monometallic Co(3)/C catalyst or alloy is formed with electron rich Pt and electron deficient Co. Based on these postulations, XRD analysis of bimetallic catalysts indicates that the Co and Pt interact with each other which may influence the geometric and/or electronic properties of metals. The diffraction peak at 26.51° (002) in carbon is assigned to the hexagonal graphitic carbon (JCPDS File No. 41-1487) and the peak at 44.64° (111) is assigned to cubic carbon (JCPDS File No. 80-0017).[61]

The oxidation states of metals in mono and bimetallic catalysts were confirmed by XPS studies (Figure 2). In the XPS spectrum of Co(3)/C catalyst sample, lack of peak for Co metal at binding energy (B.E) of 778-779 eV and observance of peaks for Co $2p_{1/2}$ (B.E.=796.2 eV) and Co $2p_{3/2}$ (B.E.=781.2 eV) are attributed to the formation of CoO and Co_3O_4 species. This inferred that in monometallic Co(3)/C catalyst, Co is present in higher (II, III) oxidation states. When monometallic Pt(3)/C catalyst was examined by XPS, strong peaks for $4f_{5/2}$ (74.5 eV) and $4f_{7/2}$ (71.1 eV) levels were observed, which signifies that the majority of Pt is present as metal [Pt(0)]. However, weak peaks for $4f_{5/2}$ (76 eV) and $4f_{7/2}$ (72.2eV) level also shows that small quantity of Pt is present as Pt(II). It can be said that the observations made with XPS analysis for monometallic catalyst

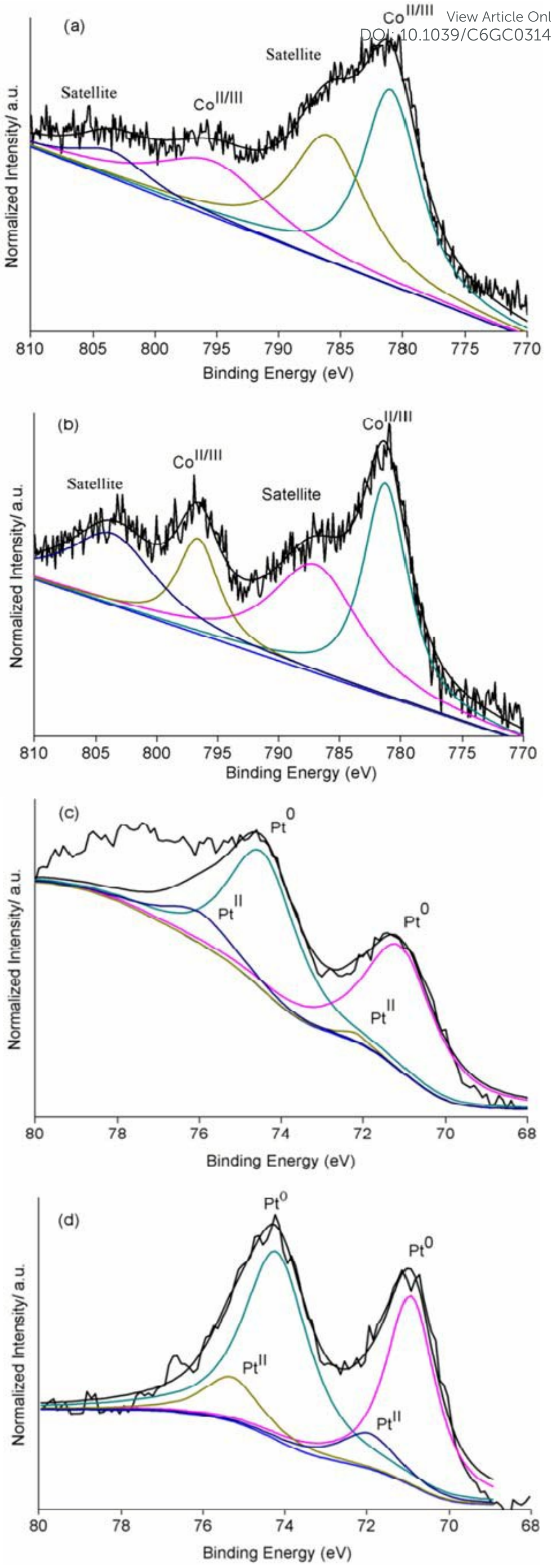

Figure 2. XPS spectra of Pt, 4f and Co 2p level (a) Co(3)/C, (b) Pt(3)Co(3)/C, (c) Pt(3)/C, (d) Pt(3)Co(3)/C

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are in line with XRD results. In the XPS spectrum for bimetallic Pt(3)Co(3)/C catalyst, characteristic peaks for Co (II, III) species were observed to be retained at 781.2 eV ($2p_{3/2}$) and 796.7 eV ($2p_{1/2}$), which confirms that even in the presence of Pt; Co is not reduced completely.[62] The peaks for Pt are shifted to lower binding energy (74.2 eV for $4f_{5/2}$ and 71 eV for $4f_{7/2}$) in bimetallic catalyst compared to monometallic Pt(3)/C catalyst. In bimetallic catalyst also weak peaks for Pt(II) species were observed (Figure 2). According to the electronegativity of the elements, Co (1.88) and Pt (2.28), the charge transfer from Co to Pt is expected which means that Pt can attract electrons from Co and thus latter remains in II and III state.[63] Generally, with an increase in electron density on metal, decrease in B.E. is observed. Considering this, our XPS results corroborate the fact that Pt becomes electron rich in bimetallic catalyst than in monometallic catalyst. It is also known fact that the core level B.E. shift, as for the noble metals, could be relatively weak (< 1 eV).[63-65] Thus from XRD and XPS results it is suggested that both, electron rich Pt and electron deficient Co are present in close proximity to each other in case of bimetallic Pt(3)Co(3)/C catalyst, reduced at 400 °C. This proximity can be explained based on either metallic Co is diluting the Pt particle or by decoration of Pt surface by Co in higher oxidation state. The likelihood of decoration is more predominant since XPS results show presence of Co in higher oxidation states. The carbon used in this study as a support has a very high BET surface area (753 m^2/g) and it is evident from Table S2 (ESI) that with increase in metal loading, surface area decreases.

Further, based on the TEM images of Co(3)/C catalyst (Figure S1, ESI), it can be commented that Co particles (8-17 nm) are well dispersed on the support. The particle size distribution and EDX spectra for Pt(3)Co(3)/C, Pt(3)/C and Co(3)/C catalysts are presented in Figure S1 (ESI). From this, it can be suggested that in bimetallic catalyst, metal particle size is average of Pt and Co catalysts.

The temperature program reduction (TPR) study was carried out to understand the reducible species of Pt and Co present in mono and bimetallic catalysts (Figure S2, ESI). In all the samples, a broad peak in the range of 343-653 °C is observed which is attributed to the reduction of oxides present on carbon and burning of carbon (CH_4).[66] As seen from TPR profile of Pt(3)/C sample, low temperature peak (180 °C) is observed for the reduction of PtO species.[67, 68] In the TPR profile of Co(3)/C catalyst, an intense peak with peak maxima at 306 °C corresponding to reduction of Co ($Co^{2+/3+}$) oxide species was seen.[69, 70] However in the TPR profile of bimetallic Pt(3)Co(3)/C catalyst, small broad peak at 265-388 °C was seen for reduction of Co. The lower intensity of this peak compared to monometallic Co(3)/C catalyst is because, in Co-Pt system, core is predominantly made up of Co and thus Co is not available for reduction. In Pt(3)Co(3)/C sample, major peak with high intensity was observed at 206 °C for reduction of Pt and Co. It is known that when Pt and Co are present in the system generally, Pt forms a shell and the peak for reduction of Pt shifts towards higher temperature. This is probably because of presence of unreduced Co as the core of particle.[68, 71-75] These observations prove that Pt and Co interact with each other.

Hydrogenation of FAL to FOL

Catalysis at 100 °C, 1 MPa H_2 pressure

As shown in Figure 3, when FAL hydrogenation reaction was carried out in iso-propyl alcohol (IPA) at 100 °C under 1 MPa hydrogen pressure with monometallic Pt(3)/C catalyst, 34% FAL conversion with 33% yield of FOL was observed. However, with the employment of bimetallic catalyst, Pt(3)Co(3)/C; substantial increase in FAL conversion (100%) and FOL yield (100%) was seen. This suggests that with bimetallic catalysts, good carbon balance was possible to achieve. To check whether this enhancement in the activity was due to Co alone, reaction was performed with monometallic Co(3)/C catalyst and we as expected observed only 3% FOL yield however with 12% conversion of FAL. This suggests that Co alone gives lower yields than bimetallic catalyst and that particle size of all the catalysts is roughly similar, it is understood that Pt and Co metals in a synergetic way facilitate the enhancement of the activity. In the literature it is acknowledged that in case of bimetallic catalysts, both the factors; geometric and electronic participate is deciding the activity of a bimetallic catalyst[43] and accordingly it is assumed that in case of Pt(3)Co(3)/C catalyst either both of these factors or either of these factors must be playing a decisive role in deciding the activity. From the XRD analysis of bimetallic catalyst it is revealed that both Pt and Co are present in close proximity with each other and from XPS study it is specified that while Pt is predominantly present in (0) oxidation state, Co is present in (II, III) oxidation states in the Pt(3)Co(3)/C catalyst. Hence it is believed that electron deficient Co may act as Lewis acid site for the adsorption of carbonyl group through oxygen atom (electron pair) of substrate, which essentially polarizes the C=O bond. At the same time, electron rich Pt(0) species would promote the heterolytic dissociation of hydrogen molecules and thus hydrogenation of the carbonyl group is facilitated.

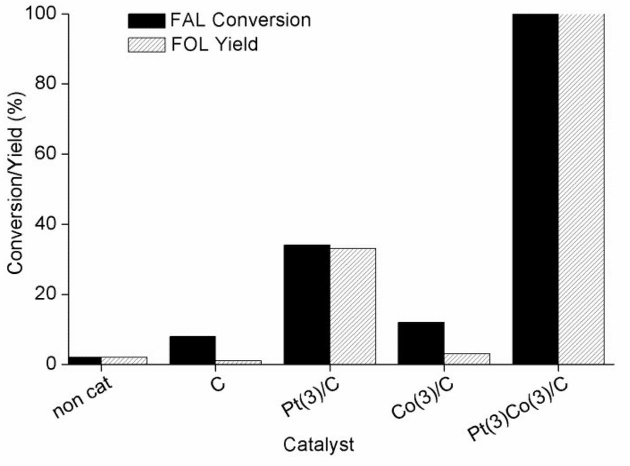

Figure 3. Effect of mono and bimetallic catalysts on the hydrogenation of FAL to FOL. Reaction condition: FAL, 0.35 g; catalyst, 0.078 g; iso-propyl alcohol, 35 mL; 100 °C; 5h; H_2, 1 MPa at room temperature; 900 rpm. FAL: Furfural, FOL: Furfuryl alcohol.

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Additionally, in monometallic Pt(3)/C catalyst, as known from the XRD and XPS studies, Pt is predominantly present in metallic (0) state and hence is electron rich however, due to this, it is difficult for FAL to interact with Pt and eventually adsorb on the Pt surface. When under similar conditions, reaction was carried out in the absence of a catalyst, <2% FAL conversion along with <2% FOL yield was seen. To understand the influence of carbon on the catalytic activity, reaction was carried out with only carbon and we observed 8% FAL conversion with 2% FOL yield. The slight increase in FAL conversion with carbon as a catalyst compared to non-catalytic reaction was because of adsorption of 4% FAL on carbon (Table S3, ESI) (checked by adsorption study carried out at room temperature) as well as formation of FAL condensation product on carbon surface in absence of active metal site as it is known from literature that FAL is unstable and undergo polymerisation reaction.[10]

To avoid the use of higher Pt concentration in the bimetallic catalyst, series of catalysts with different Pt loadings (0.5-3 *wt%*) by keeping Co concentration same (3 *wt%*) were synthesized. Amongst all these catalysts, when reactions were conducted in presence of IPA at 100 ^{o}C under 1 MPa hydrogen pressure for 5 h, Pt(3)Co(3)/C catalyst showed maximum activity 100% yield for FOL) with turnover number (TON) of 2582 (Figure S3, ESI). However, under similar conditions with Pt(2)Co(3)/C catalyst also near maximum FOL yield (92%) was obtained with TON of 4275. The higher TON with Pt(2)Co(3)/C catalyst indicates that it is more efficient catalyst than Pt(3)Co(3)/C. When reactions were performed with lower loading of Pt (0.5 and 1 *wt%*), lower selectivity for FOL was observed as found with Co(3)/C catalyst (Figure S3, ESI, Figure 3). This is because with the decrease in Pt concentration, Co catalyzed side reactions are predominant (Figure 3). Next, reactions were also performed with the catalysts having varying concentrations of Co (0.25, 0.50, 1, 2, 3, 4, 5 *wt%*) by keeping Pt concentration constant (3 *wt%*) as shown in Figure S4 (ESI). In all these catalysts, Pt(3)Co(3)/C catalyst showed best activity (100% FOL yield) and all other catalysts showed lower yields in the range of 35-90%. With higher Co concentration of 5 *wt%*, selectivity for FOL was decreased to 90% because with excess of Co in catalyst, initiation of side reactions of FAL is possible as evident from monometallic Co(3)/C catalyst result (Figure 3). Moreover, with higher concentration of Co, burial of active Pt sites is possible as it is suggested that Co may decorate Pt particles. The analogous observation is as well made when Pt concentration was altered. Thus, from these results it is inferred that Pt(3)Co(3)/C catalyst is the best catalyst to achieve highest possible FOL yield and the second best catalyst is Pt(2)Co(3)/C in terms of TON.

Catalysis at 50 °C, 1 MPa H_2 pressure

Since, selective formation of FOL was achieved at 100 ^{o}C under 1 MPa hydrogen pressure in presence of IPA as a solvent within 5 h reaction time; reaction was performed at 50 ^{o}C for 5 h under 1 MPa hydrogen pressure. In this reaction, 52% FOL yield was achieved with 100% selectivity. Considering this, next reaction was carried out for 10 h and with bimetallic, Pt(3)Co(3)/C catalyst high yield (91%) was observed. The gas phase of reactions was analyzed by GC-TCD but no detectable peak for any gaseous products was observed. As Pt(3)Co(3)/C catalyst showed very high activity even at 50 ^{o}C with 1 MPa hydrogen pressure, it was decided to carry out reactions at lower hydrogen pressure. The results imply that the activity of the catalyst is proportional to the hydrogen pressure (Figure S5, ESI).[26] Generally, with increased pressures, solubility of hydrogen is increased in solvents and it was believed that this increase in solubility might play a role in enhancing the activity.[76] However, to check the effect of overall pressure on the activity, reaction was carried out with 1 MPa N_2 pressure (instead of hydrogen) and mere 10% conversion (10 h) without formation of FOL was observed as compared with 92% conversion obtained with 1 MPa hydrogen. Further to check the role of IPA at higher temperature, reactions were carried out at 100 and 150 °C with 1 MPa N_2 pressure for 5 h. When reaction was done at 100 °C, 7% FAL conversion with no FOL formation was achieved. However when reaction was performed at 150 °C, 8% FAL conversion with 8% FOL yield was seen. The conversion at 100 °C could be due to the undesired side reaction in absence of H_2. It is also reported that at 150 °C IPA can act as proton donor.[24] This outcome implied that under our reaction conditions (<100^{o}C), i) instead of total pressure, hydrogen pressure is essential and ii) source of hydrogen is hydrogen gas and not the solvent. However, when the reaction was carried out at 0.1 MPa hydrogen pressure with increased catalyst concentration (S/C = 2.12 *wt/wt*), improvement in the FOL yield to 57% was seen compared with 12% obtained with lower (S/C = 4.35 *wt/wt*) catalyst concentration at 0.1 MPa (Figure S6, ESI). After obtaining these encouraging results with 0.1 MPa hydrogen pressure, reaction was carried out for longer time (15 h) instead of 10 h and 80% FOL yield was achieved. Nevertheless, further increase in reaction time (20 h) did not yield much improvement in FOL yield (84%). It is known that alcohols are used as proton donating solvents at higher temperatures (typically >150 ^{o}C) and thus when reactions were carried out at 50 °C in this work using IPA, it was apparent that IPA does not contribute any protons which means that solvent is not contributing (as catalytic transfer hydrogenation) towards the reaction at 50 °C. Considering this, it was decided to study the effect of solvent on the reaction. The reactions were performed at 50 $^{\circ}$C for 1 h under 1 MPa hydrogen pressure with different solvents. As shown in Table 1, compared to any organic solvent, with water as a solvent highest FOL yield (95%) with (95%) conversion of FAL was achieved within 1 h (Entry 8, Table 1). Primarily, this difference in activity is believed to be associated with the various properties of solvents such as polarity, Hansen solubility parameter(HSP), reactivity of FAL with solvent and capacity to dissolve hydrogen (Table S4, ESI). Previously, it is reported that, owing to the preferential adsorption of water compared to FAL on the catalyst surface of (hydrophilic) SiO_2 supported Cu catalyst, lower conversions are possible.[77] It is also demonstrated that due to strong adsorption of FAL on PtSn/SiO_2 catalyst in non -polar solvents,

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decrease in the activity of catalyst is possible.[43] In this study, owing to presence of hydrophobic carbon as a support it was feasible to prevent the adsorption of polar solvents (water) on catalyst and this ultimately prevents the poisoning of catalyst by water and allows FAL to adsorb and interact with the catalytically active sites on the catalyst surface.

Table 1. Solvent study for hydrogenation of FAL to FOL.

Entry no.	Solvent	FAL conversion (%)	FOL yield (%)
1	Methanol	60	33
2	Ethanol	48	40
3	1-Propanol	18	16
4	2-Propanol	17	15
5	1-Butanol	17	13
6	2-Butanol	17	11
7	Toluene	7	6
8	Water	95	95

Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; solvent, 35 mL; 50 °C, 1 h; H_2, 1 MPa at room temperature; 900 rpm. FAL: Furfural, FOL: Furfuryl alcohol. Acetal formation is seen when methanol and ethanol are used as solvents.

The other reason for improvement of yield in water might be due to increase in concentration of H_2 in water since water has a K_H value of 7.45 x 10^{-3} MPa, means it has a high capacity to dissolve H_2 than for instance compared to ethanol (K_H = 0.44 x 10^{-3} MPa) when measured at 50 °C.[78, 79] All these factors are thus responsible for observing increased activity of a catalyst in presence of water, toluene being the least polar solvent amongst all, showed lowest activity. Moreover, various alcohols (except methanol) having a polarity index between 3.9 to 4.3 showed almost similar activity. However it is well reported in the litrature that during furfural hydrogenation reaction in presence of methanol as a solvent, formation of 2-hydroxy, 1-methoxy ethyl furan can be obtained and in presence of ethanol 2-furaldehyde diethyl acetal formation is observed.[28, 31, 80, 81] Similar results were observed in this work when reactions are done in presence of methanol and ethanol. In presence of methanol solvent the conversion of FAL was 60% but the FOL yield was only 33% (Entry 1, Table 1). This lower selectivity for FOL is due to the formation of 2-hydroxy, 1-methoxy ethyl furan as side product as identified by GC-MS analysis (m/z, 142, 111, 95, 53). When reaction was carried out in presence of ethanol, the conversion of FAL was 48% and 40% yield of FOL was achieved (Entry 2, Table 1). In this case too, formation of side product, 2-furaldehyde diethyl acetal (m/z 170, 125, 97, 95) was seen. However, when reactions were carried out in presence of propanol and butanol, formation of acetal products was not observed. Also decrease in selectivity for FOL with most organic solvents was due to adsorption of FAL on catalyst surface as mentioned earlier. Yet another property of solvents namely, Hansen Solubility Parameter (HSP) also showed correlation with the activity. As summarized in Table S4 (ESI), FAL has a HSP value of 22.9 δ/MPa and FOL has HSP value of 25.6 δ/MPa. A careful look at HSP values for all the solvents divulge the fact that water is superior solvent than organic solvents for carrying out this reaction. Furthermore, amongst all organic solvents, methanol is better solvent to achieve good yields compared with other solvents due to its higher HSP value (29.7 δ/MPa) compared with FAL (22.9 δ/MPa) and FOL (25.6 δ/MPa) and other organic solvents.[82, 83]

Catalysis at 35 °C, 1 MPa, water as solvent and catalyst recycle study

When reaction was carried out in IPA for 10 h at 50 °C under 1 MPa pressure with Pt(3)Co(3)/C catalyst, 91% yield of FOL was observed (Entry 2, Table 2) and hence further reaction was performed at 35 °C for 10 h under 1 MPa hydrogen pressure. In this reaction, only 41% FOL yield over Pt(3)Co(3)/C catalyst was observed (Entry 3, Table 2). Because, earlier it was seen that compared with organic solvents, better results can be obtained with water, same reaction was performed in water and 100% FAL conversion with 100% FOL yield was achieved (Entry 4, Table 2). Hence the reactions with Pt(3)/C, Co(3)/C and Pt(3)Co(3)/C catalysts were carried out at 35 °C for 10 min. in water and results are summarized in Figure S7 (ESI). It was observed that with Pt(3)/C catalyst, 10% FAL conversion with 7% yield of FOL was obtained (161.3 min^{-1} TOF), but Co(3)/C

Table 2. Hydrogenation of FAL to FOL under 1 MPa H_2 in IPA and water solvents.

Entry no.	Time (h)	FAL conversion (%)	FOL yield (%)
1[a]	5	100	100
2[b]	10	92	91
3	10	43	41
4[c]	10	100	100

Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; iso-propyl alcohol, 35 mL; 35 °C; 10 h; H_2, 1 MPa pressure at room temperature; 900 rpm; [a] 100 °C; [b] 50 °C; [c] water 35 mL. FAL: Furfural, FOL: Furfuryl alcohol.

Table 3. Hydrogenation of FAL to FOL in water solvent.

Entry no.	Catalyst	FAL conversion (%)	FOL yield (%)
1	Pt(2)/C	22	16
2	Pt(2)Co(0.25)/C	52	48
3	Pt(2)Co(1)/C	100	95
5	Pt(1)Co(3)/C	47	40
6	Pt(2)Co(3)/C	100	95
7	Pt(2)Co(5)/C	100	95
8	Pt(3)Co(3)/C	100	100

Reaction condition: FAL, 0.35 g; catalyst, 0.078 g; water, 35 mL; 35 °C; 10 h; H_2, 1 MPa at room temperature; 900 rpm. FAL: Furfural, FOL: Furfuryl alcohol.

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catalyst showed only 1% conversion. On the other hand, bimetallic catalyst showed significant increase in yield of FOL (27%) with 28% conversion of FAL (TOF to 753.1 min^{-1}). Since at 35 °C under 1 MPa pressure, better results were obtained, subsequently, all the mono and bimetallic catalysts were evaluated under similar conditions and the results are summarized in Table 3. As summarized in Table 3, with most of the catalysts, good selectivity for FOL was achieved at 35 °C. Earlier it is reported that when reactions are conducted at 25 °C over monometallic 10 *wt%* Pt/Al_2O_3 catalysts, very high H_2 pressures (6 MPa) are required to achieve 100% selectivity for FOL formation (65% yield) though with only ca. 65% FAL conversion.[29] Compared to earlier result in this work, using bimetallic PtCo catalyst with 3 *wt%* Pt loading, 100% conversion of FAL with 100% selectivity to FOL under 1 MPa H_2 pressure could be achieved. This indicates that use of bimetallic catalysts decreases the H_2 pressure to achieve high yields of FOL.

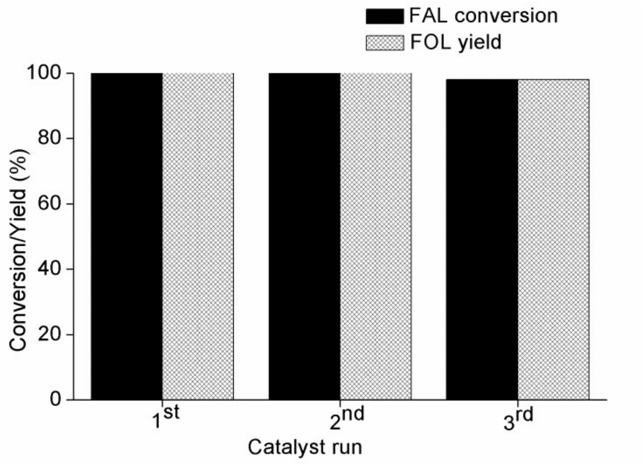

Figure 4. Recycle study of Pt(3)Co(3)/C catalyst with substrate to catalyst ratio constant. Reaction condition: FAL, 1 wt%; S/C wt ratio, 4.45; water; 35 °C; 10h; H_2, 1 MPa at room temperature; 900 rpm. FAL: Furfural, FOL: Furfuryl alcohol, S/C: substrate/catalyst

The catalyst recycle study was performed with Pt(3)Co(3)/C catalyst after separating catalyst from reaction mixture by centrifugation and again charging the wet catalyst (without weighing) in the next run. The results indicated that after each cycle, activity was dropped by ca. 10% mostly due to handling loss of catalyst which changed the S/C ratio (Figure S8, ESI) and also due to leaching of Co metal. However, catalyst was active at least until 4th runs and showed >99% selectivity for FOL formation. Later, catalyst recycle study was performed after drying the recovered catalyst. Due to this, it was possible to maintain the S/C ratio constant in all the reactions. The results obtained in these reactions are presented in Figure 4 and as seen, catalyst showed similar activity until 3rd run.

catalysis at 35-100 °C, 1 MPa, water as solvent with 1 *wt%* FAL solutions

In order to study the effect of temperature on the conversion of FAL to FOL, reactions were carried out under different temperatures for 1 h. The result shows that when reaction was done at 35 °C, the 81% conversion with 100% selectivity of FOL could be achieved (Entry 1, Table 4). However reaction carried out at 50 °C showed 95% conversion with 100% selectivity (Entry 2, Table 4) and at 100 °C, complete conversion with 100% selectivity of FOL was observed (Entry 3, Table 4). This shows that with an increase in temperature, rate of conversion of FAL increases. This can be because of increase in solubility of FAL in water.

Table 4. Effect of reaction temperature on the hydrogenation of FAL to FOL in water as a reaction medium.

Entry no.	Temperature (°C)	FAL conversion (%)	FOL yield (%)
1	35	81	81
2	50	95	95
3	100	100	100

Reaction condition: FAL, 0.35 g, Pt(3)Co(3)/C, 0.078 g; water, 35 mL; 1 h; H_2, 1 MPa pressure at room temperature, 900 rpm. FAL: Furfural, FOL: Furfuryl alcohol.

Catalysis at 35-100 °C, 1 MPa, water as solvent with 5-40 *wt%* FAL

Literature suggests that mostly these reactions are carried out with <10 *wt%* FAL solutions, however as mentioned earlier, industries would prefer to use concentrated substrate solutions to achieve better economics. Considering this, reactions were carried out with concentrated FAL solutions and the results are summarized in Table 5. When the reaction was carried out with 5 *wt%* FAL solution, 98% conversion with 98% yield of FOL was observed (Entry 1, Table 5). Later, reaction was carried out with 20 *wt%* FAL solution and 50% conversion with 49% yield of FOL was achieved (Entry 2, Table 5). Since in this reaction, selectivity was good but conversion was less, further reaction was carried out at 50 °C with 20 *wt%* FAL solution for 6 h. In this reaction, 100% conversion with

Table 5. Effect of FAL concentration on the hydrogenation in water as a reaction medium.

Entry no.	FAL (*wt%*)	Temperature (°C)	Time (h)	FAL conversion (%)	FOL yield (%)
1[a]	5	35	10	98	98
2	20	35	10	50	49
3	20	50	6	100	100
4	40	50	6	100	86
5	40	100	3	83	28

Reaction condition: FAL; Pt(3)Co(3)/C; Substrate/Catalyst ratio, 4.45 (*wt/wt*); water, 35 mL; H_2, 1 MPa pressure was maintained during the reaction by charging H_2 intermittently; 900 rpm; FAL: Furfural, FOL: Furfuryl alcohol. [a] H_2, 1 MPa was charged at room temperature and during reaction no additional H_2 was charged in the reactor.

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100% FOL yield was obtained (Entry 3, Table 5). Further reaction was carried out with 40 *wt%* FAL (8 g FAL in 20 mL water) at 50 °C under 1 MPa H_2 pressure for 6 h. In this reaction, 86% yield of FOL with 100% conversion of FAL was observed. It is known from the literature that at 25 °C, the solubility of FAL in water is only 8% and that of FOL is infinite.[84] However, it is also reported that solubility of FAL increases to infinite above 120 °C.[85] Since, in this work reactions were carried out at 50 °C, solubility study of 40 *wt%* FAL and FOL was carried out in water at room temperature and similar results as that with literature could be seen (Table S4, ESI). This may create a biphasic system in the reactor when reactions are done with higher concentrations of FAL. Considering this limitation of lower solubility of FAL in water, it was thought that reactions can be done at higher temperature to increase the solubility of FAL in water which would in turn improve the yield and reaction rate. Hence, reaction was carried out at 100 °C for 3 h with 40 *wt%* FAL solution. It was observed that although conversion of FAL reached up to 83% under reaction conditions but, only 28% yield of FOL could be achieved. This suggests that when higher concentration solutions are used, it is better to carry out reactions at lower temperatures or else side reactions become predominant. These results (Entries 3 and 4, Table 5) also revealed that even if at lower reaction temperatures biphasic system is formed, it does not have any substantial effect on the product formation

Catalysis at 35 ^{o}C, 0.1 MPa and water as solvent

The ultimate aim of carrying out any chemical reaction is to perform the reaction under ambient conditions and hence reaction with optimized catalyst, Pt(3)Co(3)/C was carried out in water as a solvent at 35 ^{o}C under 0.1 MPa hydrogen pressure for 10 h and a very promising result of 100% FAL conversion with 100% yield of FOL was obtained as shown in Table 6. In order to reduce the reaction time under lower H_2 pressure (0.1 MPa H_2) reaction was carried out at higher temperature (100 °C) for 4 h and 100% conversion of FAL with 100% yield of FOL was achieved (Entry 4, Table 6). After the reaction was carried out under optimized reaction condition [Pt(3)Co(3)/C, 35 °C, 0.1 MPa hydrogen, 10 h, water] product, FOL was extracted from water using ethyl acetate. Later this recovered FOL was dissolved in $CDCl_3$ and the ^{13}C & ^{1}H NMR spectra were recorded to check its purity. The chemical shift values observed in the NMR spectra (Figures S9 and S10, ESI) matched well with the literature.[86, 87] These results reveal that FOL is obtained in pure form which again indicates that 100% selectivity was obtained in these reactions. Further, in HPLC profile (Figure S11, ESI) single peak for FOL was seen which again indicates that FOL is obtained in pure form.

Table 6. Hydrogenation of FAL to FOL in water as a reaction medium and under ambient conditions (35 ^{o}C, 0.1 MPa H_2 pressure).

Entry no.	Time (h)	FAL conversion (%)	FOL yield (%)
1	5	65	63
2[a]	5	83	72
3	10	100	100
4[b]	4	100	100

Reaction condition: FAL, 0.35 g; Pt(3)Co(3)/C, 0.078 g; water, 35 mL; 35 °C, H_2, 0.1 MPa at room temperature, 900 rpm. [a] catalyst, 0.16 g; [b] 100 °C; FAL: Furfural, FOL: Furfuryl alcohol.

Proposed reaction mechanism

From the study of FAL conversion to FOL in presence of bimetallic catalyst it is proposed that Pt(0) facilitate the heterolytic splitting of the H_2 molecule into H^+ and H^-. The oxophilic Co(II) ion attracts the carbonyl oxygen and polarizes the carbonyl group of FAL which increases the interaction between catalyst and FAL. The proposed reaction mechanism is shown in Figure S12 (ESI).

Characterization of spent catalyst

Pt(3)Co(3)/C spent catalyst obtained from the reaction (35 °C, 0.1 MPa H_2, 10 h, water) was characterized by XRD, XPS, TEM, ICP and BET surface area techniques to check the morphology. XRD pattern of Pt(3)Co(3)/C spent catalyst as shown in Figure S13, (ESI) shows the peak for PtCo alloy species at the same position as observed in fresh catalyst. The defractogram of fresh catalyst is matching with the spent catalyst. From the XPS analysis (Figure S14, ESI) shift of 781 eV peak of Co (II) to 782 eV position for Co 2p level was seen, this might be due to oxidation of Co in water medium, The deconvolution spectrum of Pt 4f level shows that major amount of Pt is still present in (0) oxidation state with small amount of Pt(II). TEM image of spent catalyst given in (Figure S15, ESI) shows well dispersion of particle with particle size distribution between 7 to 13 nm as observed in fresh catalyst without sintering of particles. The BET surface area of spent catalyst was found to be (635 m^2/g) which is similar to the fresh catalyst (630 m^2/g). An ICP analysis of spent catalyst showed absence of any leaching of Pt metal however, slight loss of Co metal (1.94 ppm) was observed. Almost similar amount of Co was quantified in the reaction solution.

Experimental Section

Catalyst synthesis

Supported mono (Pt/C, Co/C) and bimetallic (PtCo/C) catalysts were prepared by wet-impregnation method. Before synthesis of catalyst, carbon (s. d. fine chemicals, having surface area 753 m^2/g) was activated at 150 °C for 6 h. In a typical procedure, 1 g of activated carbon was immersed in 10 mL of water and the mixture was kept under stirring for 30 min. To this, 2.50 mL aqueous solution of $Pt(NH_3)_4(NO_3)_2$ (Alfa Aesar 99.99% purity) containing 30 mg of Pt was drop wise added and the resultant mixture was stirred for 16 h at room temperature. This is followed by evaporation of water at an elevated temperature 60 °C using rotary evaporator. The

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powder obtained was dried at 60 °C in oven for 16 h followed by vacuum drying at 150 °C for 6 h. Further this dry catalyst powder was reduced in a flow of hydrogen (H_2, 10 mL/min) for 2 h at 400 °C to obtain Pt(3)/C catalyst. A monometallic Co(3)/C catalyst was prepared using aqueous solution of $Co(NO_3)_2{\cdot}3H_2O$ (Thomas Baker, 97% purity) following same procedure as mentioned above. Bimetallic PtCo/C catalysts containing 0.5, 1, 2 and 3 *wt%* and 2 *wt%* Pt and 0.25, 0.5, 1, 2, 3, 4, 5 *wt%* of Co were prepared by co-impregnation method. A catalyst with 3 *wt%* Pt and 0.25 *wt%* Co loading was named as, Pt(3)Co(0.25)/C. Similarly, all other catalysts were named based on their loadings.

Characterization of catalyst

The monometallic Pt/C, Co/C and bimetallic PtCo/C catalysts were characterized by XRD, N_2 sorption, TEM, ICP-OES and XPS, TPR techniques. XRD spectra were obtained using PANanalytical X'pert Pro, Netherlands; with duel goniometer diffractor equipped with a Cu Kα (1.5418 Å) radiation source with Ni filter. Data were collected in the 2θ range of 5–90° with a step of 4°/min and 30-50° with a step of 1°/min. N_2 physisorption experiments were done at -196 °C in a Autosorb 1C Quantachrome instrument, USA. Prior to analysis, samples were activated under vacuum at 200 °C for 3 h. The specific surface area was determined by BET method and pore size was calculated by BJH method. The electronic states of metals were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PH 15000C) having x-ray source Al Kα radiation. The mode of lens was LAXPS and Energy Step Size 0.1 eV. Peak in the spectrum were deconvoluted by XPSPEAK-41. All binding energy values were calibrated using the value of carbon (C1S = 284.4 eV) as a reference. TEM images were obtained using FEI TECNAI T20 model instrument working at an accelerating voltage of 200 kV. Samples were dispersed in iso-propyl alcohol (IPA) by sonication and the drop casted on carbon coated copper grid. Metal contents in the catalysts were determined by ICP-OES analysis using 'SPECTRO ARCOS Germany, FHS 12' instrument. Samples were prepared by calcining catalyst at 600 °C (5 °C/min ramping rate) for 6 h in air atmosphere and solid residue after calcination was dissolved in aquaregia. All ICP-OES samples were diluted with deionized water and filtered (through 0.22 µm syringe filter) before analysis. The TPR studies were done by Micromeritics Autochem-2920 instrument in the temperature range 50−800 °C in presence of 5% H_2 in He with a ramping rate of 5 °C/min. The catalyst was treated at 300 °C for 1 h in presence of He gas before the TPR analysis. The measurement of H_2 consumption in the TPR analysis was done by a thermal conductivity detector (TCD) instrument.

Catalytic runs

Hydrogenation of furfural (FAL) was performed in a 50 mL stainless steel high pressure high temperature Amar make reactor by charging 35 mL solvent, 0.35 g FAL and 0.078 g catalyst. The reactor was flushed with H_2 for four times to remove any air. Then, the reactor was pressurised with H_2 up to desired pressure (0.1-1 MPa) and was heated slowly (3 °C/min) until desired temperature (35-100 °C) is reached under slow stirring (100 rpm). After attaining the reaction temperature, stirring was increased to 900 rpm and this time was considered as starting time of the reaction. Sample was withdrawn and quantification of furfural was done to ascertain the conversions and yields.

Recycle experiments

After completion of a reaction, the catalyst (solid) was recovered by centrifugation of reaction mixture. The recovered wet catalyst was used in the next reaction without any pre-treatment. Also in order to check the activity of catalyst by maintaining substrate to catalyst ratio constant the moisture of recovered wet catalyst was removed by drying at 60 °C for 12 h followed by 150 °C for 3 h after each recycle run. The dried catalyst was used to carry out next reaction without further treatment.

Analysis of the reaction mixture

After completion of reaction, reactor was allowed to cool to room temperature under flow of air. Later reactor was immersed in ice bath for (30 min). The reaction mixture was collected and centrifuged to separate solid and liquid. The liquid was filtered through 0.22 µm syringe filter. Analysis of organic reaction mixture was done using gas chromatography (Varian GC) attached with FID for calculation of FAL conversion, and selectivity of FOL. The conditions used for GC analysis were as follows: HP-5 capillary column (0.25 µm x 0.32 mm x 30 m), a FID detector (30 mL/min N_2 flow as a carrier gas, 250 °C), and the oven temperature programme was as follows: 50 °C (hold time 1 min) to 200 °C (hold time 10 min) at the rate of 15 °C/min ramp rate. Injector temperature used was 200 °C. The GC-MS (Agilent-7890 GC and Agilent MS-5977A MSD) equipped with DB-MS column (0.25 µm X 0.25 mm X 30 m) was used for the analysis. The temperature programs used were similar to that for GC-FID. NIST library was used for the identification of products. The HPLC (Agilent Technologies, 1200 infinity series, USA) equipped with an HC-75 Pb^{2+} column (Hamilton, 7.8 mm × 300 mm, 80 °C) and refractive index detector (Agilent Technologies, 1200 infinity series, 40 °C) was used to analyze aqueous reaction mixture. HPLC grade water was used as an eluent, at a flow rate of 0.5 mL/min. FAL conversion and product FOL yields were calculated on mole basis using the following formulae.

$$\begin{array}{c}\text{\% Conversion of}\\ \text{Furfural}\end{array} = \left[\frac{\text{Initial mole of Furfural - Final mole of Furfural}}{\text{Initial mole of Furfural}}\right] X100$$

$$\text{Yield} = \left[\frac{\text{Mole of product formed}}{\text{Theoreticle mole of product}}\right] X\ 100$$

TOF an TON are calculated by using following formula

$$\mathrm{TOF} = \left[\frac{\text{mole of substrate converted}}{\text{mole of active site X time}}\right] \mathrm{X}\ 100$$

$$\mathrm{TON} = \left[\frac{\text{mole of substrate converted}}{\text{mole of active site}}\right] \mathrm{X}\ 100$$

mole of active sites of Pt were calculated by TEM analysis

Extraction of Product

Extraction of product FOL was done by solvent extraction method using ethyl acetate as solvent. The mass obtained after evaporation of ethyl acetate using rotary evaporator was dried in oven at 60 ^{o}C for 6 h to remove any remaining solvent. The 15 mg dried mass was dissolved in $CDCl_3$ to record ^{1}H NMR and ^{13}C NMR spectrum of the obtained mass. A ^{1}H NMR of extracted FOL was taken on Bruker Ascend instrument at 200 MHz in deuterated chloroform ($CDCl_3$). TMS was used as internal standard for the analysis. The ^{13}C NMR was taken on 50.32 MHz instrument in deuterated chloroform. The number of scan used for ^{1}H and ^{13}C NMR were 8 and 1000 respectively.

Conclusions

In this work we have shown that by carefully designing a catalyst with optimum combination of electron rich and deficient metals can be useful in achieving maximum yield of FOL (100%) from FAL under ambient conditions (35 ^{o}C, 0.1 MPa H_2) in water media. The maximum possible yield of FOL (100%) observed in these reactions carried out at 50 ^{o}C with high substrate concentration (20 *wt%*) is industrially relevant Additionally, good FOL yield of 86% was observed when 40 *wt%* FAL solution is used in the reactions. The catalyst can be recyclable up to 4th run with marginal loss of activity due to leaching of Co metal and also due to oxidation of Pt and Co. The impregnation of Pt and Co on carbon (C) as support also helps in attaining highest activity as poisoning of catalyst by water is not possible due to hydrophobic nature of support. The complete characterization of fresh and spent catalysts discloses the information on the morphology and electronic properties of the catalyst which later are correlated with activity of catalysts. This work shows simple, clean and efficient process for industrial application in conversion of FAL to FOL with higher substrate concentration in water medium at lower H_2 pressure ever reported with better selectivity.

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Keywords: furfural • furfuryl alcohol • co-impregnation • hydrogenation • aqueous phase

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