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Conversion of furfuryl alcohol into 2-methylfuran at room temperature using Pd/TiO_2 catalyst

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The selective hydrogenation of furfuryl alcohol into 2-methylfuran was investigated at room temperature using palladium supported catalysts. We have shown that Pd–TiO_2 catalysts can be very effective for the synthesis of 2-methylfuran at room temperature and low pressure of hydrogen (1–3 bar). The effect of various reaction conditions (pressure, catalyst amount, and solvent) was studied.

Introduction

One of the most plentiful resources of renewable energy that exists in the world is biomass. The current challenge for researchers in both industry and academia is the development of efficient technologies that utilize biomass or biomass-derived chemicals to a large extent.[1–4] The platform molecules that feature in a large proportion of the current research are based on intermediates such as 5-hydroxymethylfurfural (HMF), furfural, furfuryl alcohol (FA), gamma valerolactone (GVL), and attractive bio fuels *e.g.* 2-methyl furan (2-MF), and 2-methyltetrahydrofuran (2-MTHF).[1,5–7] HMF is considered as one of the most versatile molecule for a number of reasons. All the 6 carbon atoms originally present in hexoses are retained in this molecule, and can be prepared with high selectivity from fructose. It is a parent molecule of many useful chemicals like caprolactone,[8] 2,5-dimethylfuran,[9] 2,5-furandicarboxylic acid[10] *etc.*

Furan derivatives are considered to be important intermediates because of their rich chemistry with carbohydrates being the most dominant source of these platform molecules. Recently, efforts have been made in the conversion of carbohydrates into furan derivatives in the form of furfural and furfuryl alcohol.[11–14] One of the methods used to get fuels from the renewable feedstock resource is by its pre-treatment through hydrolysis of the cellulosic and hemicellulosic components to produce sugar alcohols, such as sorbitol, xylitol, mannitol, lactitol or maltitol[15–20] which are consequently converted into fuel components *via* chemical reactions.[21–24] Furfuryl alcohol is an important bio-derivative obtained from hydrogenation of furfural-a product of xylose. This compound has shown a variety of applications in chemical industry.[25–32] A schematic pathway is shown in Fig. 1 for the synthesis of various derivatives from lignocellulose. There are some studies reported on conversion of furfuryl alcohol into various fuel derivatives *e.g.* 1,5-pentanediols,[33] tetrahydrofurfuryl alcohol,[34] and methyl furan.[4] All these derivatives are important in terms of their application, but their synthesis under green conditions represents a significant challenge. 2-MF is obtained from the hydrogenation of FA and furfural. It is mainly used for the synthesis of crysanthemate pesticides, perfume intermediates, and chloroquine lateral chains in medical applications.[35,36] Almost all the reported work on FA hydrogenation is performed using harsh reaction conditions. Adkins *et al.*[33] in 1931, for the first time reported the hydrogenolysis of FA using a copper chromite catalyst. The reaction was carried out in the liquid phase for 11.5 h at 100 °C and 100–150 bar pressure hydrogen. They reported a yield of 70% to pentanediol under these conditions. Pure Energy Corporation patented a process for the synthesis of 2-MF using chromium-based catalysts.[37] The main problem with chromium catalysts is toxicity which causes severe environmental pollution.[25] Dunlop and Schegulla[34] patented a process for transforming FA into tetrahydrofurfuryl alcohol with a nickel-based catalyst. Nickel catalysts have been reported to be selective for the synthesis of tetrahydrofurfuryl alcohol from FA under very harsh reaction conditions[29,38,39] (180 °C, and 3.5 h). Sitthisa *et al.*[4] have reported hydrogenation of FA with Ni–Fe/SiO_2 catalyst at 250 °C, 1 bar, with high selectivity to 2-MF and furan. Increasing the loading of nickel increased the selectivity to 2-MF. Zhu *et al.*[40] have reported an efficient synthesis of 2-MF and GBL over copper-based catalysts from furfural at 240 °C. Ruthenium metal is known to be an active hydrogenation catalyst for a number of hydrocarbons. Zhang *et al.*[29] have reported the catalytic activity of Pt, Pd and

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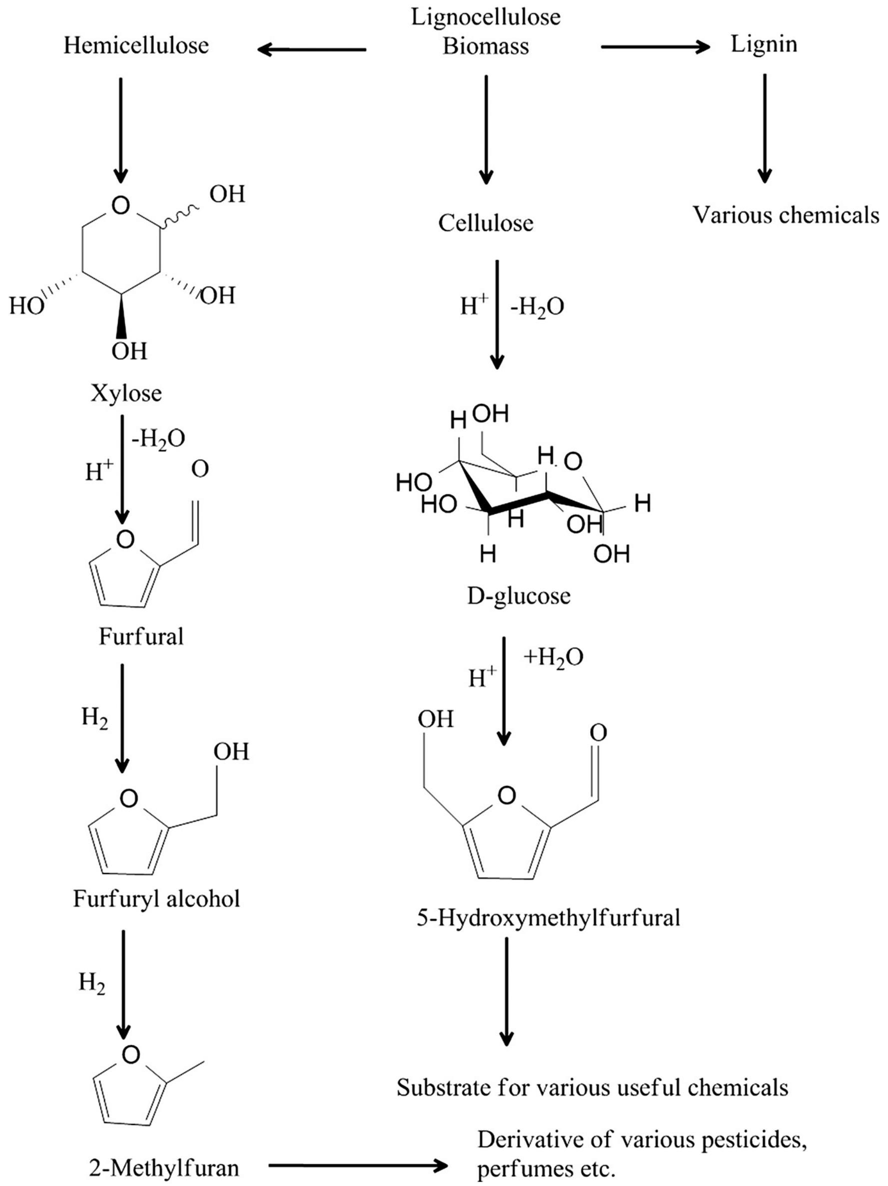

Fig. 1 Reaction pathway for the formation of various derivatives from lignocellulose biomass.

Ru supported on MnO_x for the hydrogenation of FA at 120 °C, 30–60 bar, for 4 h in an aqueous phase. A high selectivity of tetrahydrofurfuryl alcohol was achieved using Pd/MnO_x and Rh/MnO_x catalysts. The Ru/MnO_x catalyst was reported to be more selective towards 1,2-pentanediol under these reaction conditions. Pd, Rh, and Pt supported catalysts are reported to be less active compared with nickel even at higher temperature and pressure.[41,42] Zhong *et al.*[35] have reported 85% yield of 2-MF from furfural at 212 °C with copper-based catalysts. These observations show that a process for the selective synthesis of 2-MF under green reaction conditions is a challenge, because of the possibility of formation of various by products. In the current work we report an application of Pd-supported catalyst synthesized by wet impregnation method in selective biomass hydrogenation and we discuss the catalytic performance of Pd catalysts under different reaction conditions such as variation in pressure, solvent and amount of catalyst on the hydrogenation of FA at room temperature. The unique catalytic activity and preferable selectivity to hydrogenated deoxygenation of C=O, and not the reduction of C=C in this kind of furan substrates has not been reported before, under green conditions.

Experimental

Materials

Furfuryl alcohol (98%), 2-methylfuran (98%), 1, 2-dichloroethane (98%), and all the intermediates were purchased from Sigma Aldrich and used as received. Palladium chloride was purchased from Johnson Matthey. Titania was purchased from Degussa. Pure hydrogen (99.9%) was from BOC, 5% Pd/Al_2O_3 was purchased from Johnson Matthey.

Catalyst preparation

Incipient wetness impregnation method. Catalysts supported on titania were prepared using the standard wet impregnation method. The preparation of desired loading of 1, 2.5, and 5% Pd on titania is described as follows (all quantities stated are per g of finished catalyst). $PdCl_2$ (0.0166 g, Johnson Matthey) was added to deionised water and stirred at 80 °C until the Pd dissolved completely. The support (0.99 g; titania (Degussa)) was added to the solution and stirred to form a paste. The paste was dried (110 °C, 16 h) and calcined in static air (400 °C, 3 h). The MP-AES analysis showed less amount of Pd on support, so the actual loading is discussed in all relevant sections.

Characterization

Microwave plasma atomic emission spectroscopy (MP-AES). The actual metal loadings were performed using Agilent 4100 MP-AES (Microwave Plasma Atomic Emmision Spectroscopy) for all catalysts. About 5 mg catalysts were digested using 20% *aqua regia*, and all the particles in the solution were removed before the analysis.

X-ray diffraction (XRD). Powder XRD was carried out using a PANalytical X'Pert Pro with a CuK_α X-ray source run at 40 kV and 40 mA fitted with an X'Celerator detector. Each sample was scanned from 2θ = 10 to 80 for 30 min. The catalysts were ground into fine powder form and loaded on a silicon wafer. The results obtained were compared with the information in ICDD library for each catalyst.

High resolution transmission electron microscopy (HRTEM). Transmission electron microscopy (TEM) was performed on a Jeol 2100 microscope operated at 200 kV fitted with an Oxford Instruments EDX analyser. Samples were prepared by dispersion in methanol and dropped on to holey carbon film, 300 mesh copper grids. Particle size distributions (PSD) were determined by counting 150 particles using Image J software.

X-ray photoelectron spectroscopy (XPS). Samples were characterized using a Kratos Axis Ultra-DLD photoelectron spectrometer, using monochromatic Al K_α radiation, at 144 W (12 mA × 12 kV) power. High resolution and survey scans were performed at pass energies of 40 and 160 eV respectively. Spectra were calibrated to the C (1s) signal for adventitious carbon at 284.7 eV and quantified using CasaXPS v2.3.15, utilizing sensitivity factors supplied by the manufacturer.

Catalytic testing

Furfuryl alcohol hydrogenation. The reactor was charged with furfuryl alcohol (1 g), dichloroethane (20 ml) and catalyst (0.1 g). The autoclave was sealed, pressurised with hydrogen (1–3 bar, continuously controlled or constant pressure), and stirred (1000 rpm) for 30–120 min at room temperature. The reaction mixture (after centrifuging the sample to isolate the catalyst) was analysed by GC (Varian 3800 fitted with CP wax column). Products were identified by comparison with authentic samples. For the quantification of the amounts of reactant consumed and products generated, an external calibration method was used. External standard was acetonitrile.

Results and discussion

Effect of palladium loading

Various loadings of palladium metal supported on titania have been studied and a variation in activity of catalysts is observed with respect to conversion and selectivity both. The results are presented in Table 1. An increase in loading of Pd metal from 0.50% to 2.58% increases the activity of catalyst and selectivity to 2-MF. The reactions were performed at room temperature and hydrogen pressure was 1 bar (constant pressure). The side product was tetrahydrofurfuryl alcohol.

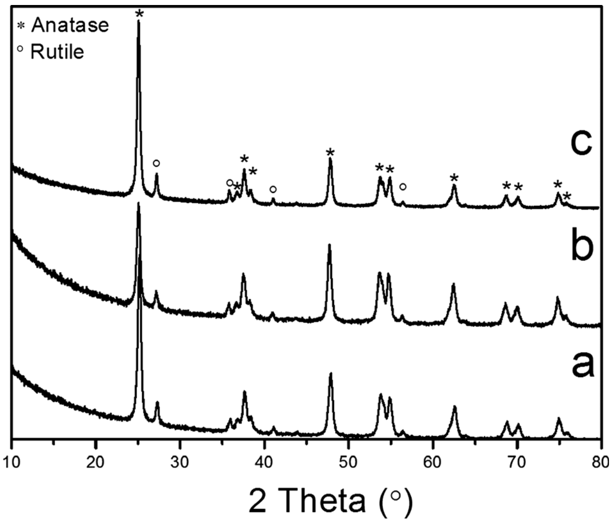

Fig. 2 XRD patterns of TiO_2 supported Pd with different loading. a. Pd = 0.50%, b. Pd = 1.26%, c. Pd = 2.58%.

Table 1 Effect palladium loading on catalysis for hydrogenation of furfuryl alcohol[a]

		Selectivity (%)		
Catalysts	Conversion (%)	2-Methylfuran	Tetrahydrofurfuryl alcohol	TON h^{-1}
0.50% Pd/TiO_2[b]	21.4	49	5.1	76
1.26% Pd/TiO_2	46.2	92.5	7.5	124
2.58% Pd/TiO_2	65.1	85.2	13.8	80
5% Pd/Al_2O_3[b]	100	17	—	12

[a] Reaction conditions: substrate (1 g), catalyst (100 mg), $C_2H_4Cl_2$ (20 ml), autoclave reactor, 25 °C, 3 h, 1000 rpm, 1 bar H_2. [b] Rest of the products are dimers. TON = Turn over number.

Blank reaction, and the reaction with pure titania showed no conversion under these conditions. One commercial catalyst 5% Pd/Al_2O_3 was also tested in order to make a comparison with titania but it showed very poor selectivity to the desired product and the main products were polymerized hydrocarbons.

The XRD pattern of supported Pd catalysts with different loadings is shown in Fig. 2. No significant difference was observed from 0.50 wt% to 2.58 wt% Pd loading and no peak can be assigned to diffraction of crystalline Pd particles. The TiO_2 used in present work is mixture of anatase and rutile, which keeps stable during preparation process. It suggests no big particles of Pd compounds (metallic Pd or PdO) are formed during preparation.

Particle size of the metal nanoparticles in these supported catalysts is an important parameter which can affect the activity. Fig. 3 shows TEM images for catalysts with 0.5%, 1.26% and 2.58% Pd/TiO_2. We did not find any large palladium particles in microscopic images. It keeps a good agreement with XRD results. In the HRTEM images, very small particles were observed in abundance in all three samples, which cannot be identified by XRD due to their lower mean particle size (<2 nm). This combined with the XRD results, means the impregnation method produces very small nanoparticles (<2 nm). In this case we tried to identify detailed information about the smaller particles we observed in the localized TEM images considering that the smaller particles might have higher activity for the catalytic results.[43–45] The particle size distribution of the three Pd catalysts with different loading were analysed. As can be observed in Fig. 3 there is very little difference in the particles size with increased loading, with all catalysts displaying an average particle size in the order of 1 nm. Given the uniformity of particle size

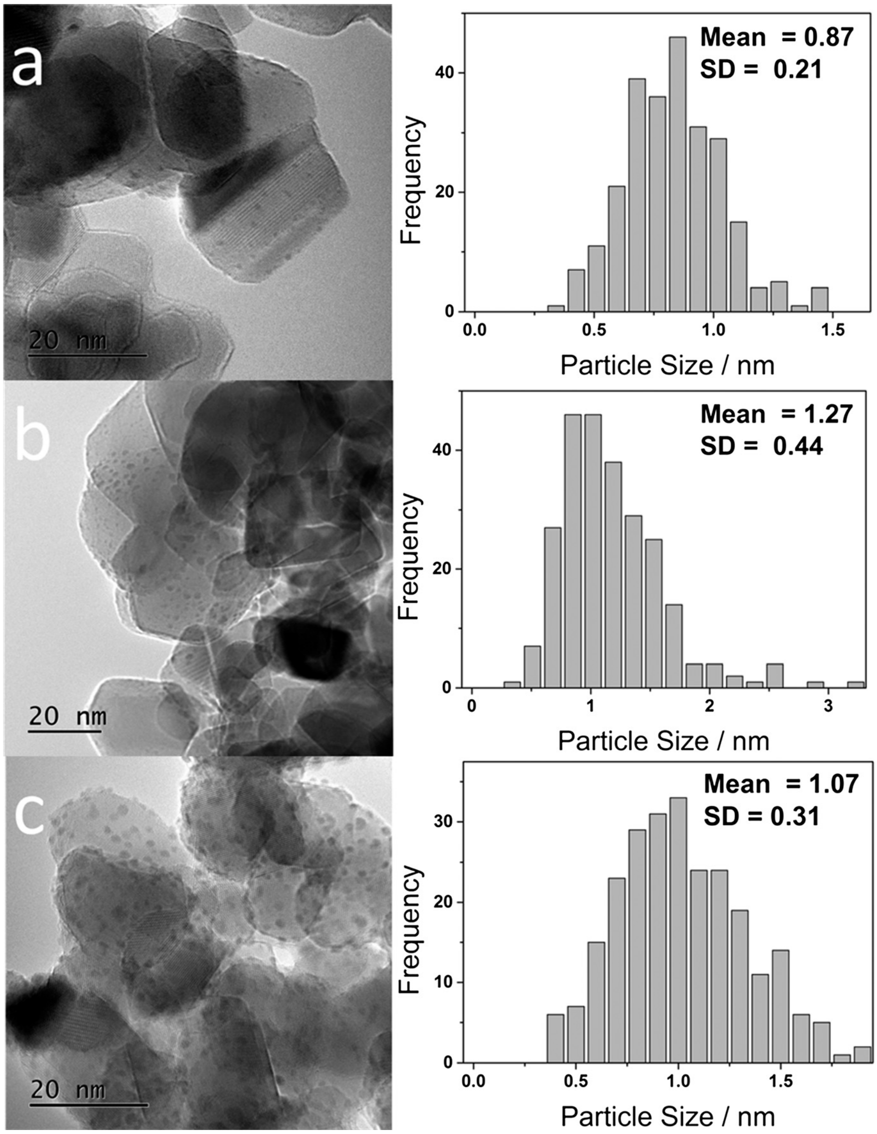

Fig. 3 Transmission electron micrographs and particle size distribution for titania supported palladium catalysts; a) 0.5% $PdTiO_2$, b) 1.26% $PdTiO_2$, c) 2.58% $PdTiO_2$.

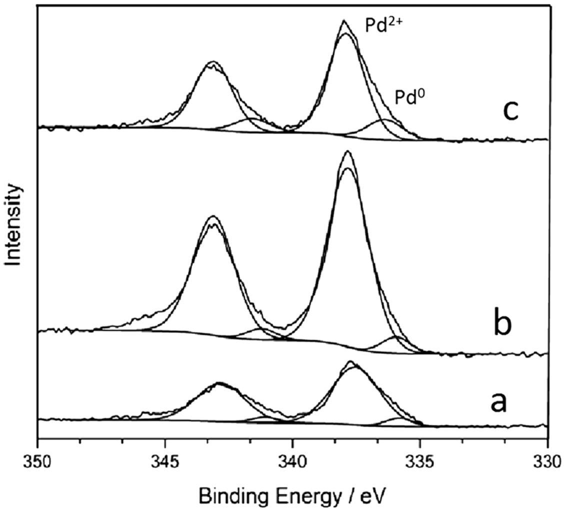

Fig. 4 XPS profiles of TiO_2 supported Pd with different Pd loading. a. Pd = 0.50%, b. Pd = 1.26%, c. Pd = 2.58%.

distribution the increase in catalytic activity can be linked to the increase in active metal concentration and consequently the availability of active sites.

Fig. 4 shows deconvoluted XPS profiles of TiO_2-supported Pd catalysts with different loadings of Pd. Clearly, two species of Pd are observed to be present on the surface of these catalysts, one is Pd^{2+} and another is Pd^0, with binding energies of 337.6 eV and 335.8 eV, respectively. In all Pd/TiO_2 catalysts Pd^{2+} is the majority species and there is only trace amount of metallic Pd. In different samples, the ratio of Pd^{2+} to Pd^0 is maintained, ranging from 12 to 15. The predominant presence of Pd^{2+} suggests active sites might not be metallic Pd, but Pd cations, which might have a similar function like co-ordinated metal centres for H_2 activation and reduction of carbonyl group.[46] It also explains why C=O, not C=C, is preferably reduced since metallic Pd is preferably active for C=C bond reduction. Despite of different loading, a similarity in chemical nature of three supported Pd samples was confirmed by XRD, HRTEM and XPS. It suggests the change in catalytic performance should only be related with the amount of same activity sites.

In order to examine the stability of catalyst during reaction an analysis of metal loading was performed using MP-AES, the results are shown in Table 4. There is no remarkable leaching observed in all three catalysts.

Reaction conditions

Effect of hydrogen pressure. 2.58% Pd/TiO_2 was tested at varying pressures of hydrogen from 1 to 3 bar at room temperature. Separate studies were performed with constant pressure (*reactor was charged at desired pressure without refilling during the reaction*) and continuously controlled pressure (*pressure maintained throughout reaction*). The reactions were performed for 30 min. In constant pressure reactions less conversion was observed overall compared with the continuously controlled pressure reactions as shown in Table 2. This could be because of the fact that more hydrogen was available in the latter case and the amount of hydrogen was limited in constant pressure reactions.

A further increase in pressure from 1 to 3 bar in case of continuously controlled pressure showed an enhancement in activity of FA hydrogenation in both cases. At 3 bar continuous pressure almost full conversion was observed with very high selectivity to 2-MF. The only by-product detected was tetrahydrofurfuryl alcohol. So the amount of hydrogen available in the environment is an important factor for achieving higher selectivity.

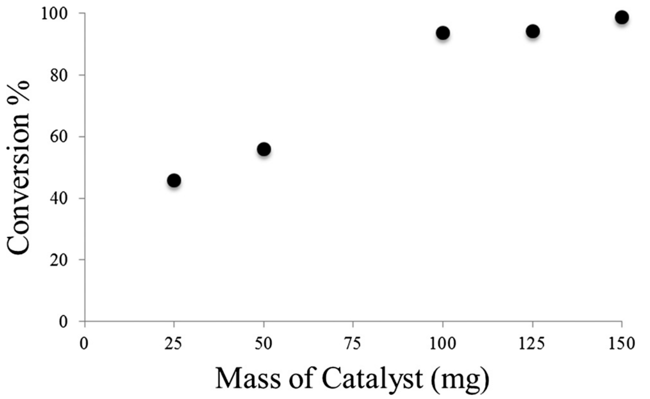

Fig. 5 Effect of catalyst mass on the conversion of FA. Reaction conditions: 1000 mg of substrate, 20 ml $C_2H_4Cl_2$, autoclave reactor, 25 °C, 30 min. 1000 rpm, 3 bar.

Table 2 Effect of hydrogen pressure on palladium catalysts for the hydrogenation of furfuryl alcohol[a]

				Selectivity (%)	
	Pressure (bar)	Time (min)	Conversion (%)	2-Methylfuran	Tetrahydrofurfuryl alcohol
Constant pressure	1	30	28.5	97.7	2.3
	2	30	50.3	97.7	2.3
	3	30	73.1	96.6	2.8
Continuously controlled pressure	1	30	54.9	98.2	1.8
	2	30	53.1	96.8	3.2
	3	30	93.7	93.6	5.7

[a] Reaction conditions: substrate (1 g), 2.58% Pd/TiO_2 (100 mg), $C_2H_4Cl_2$ (20 ml), autoclave reactor, 25 °C, 1000 rpm

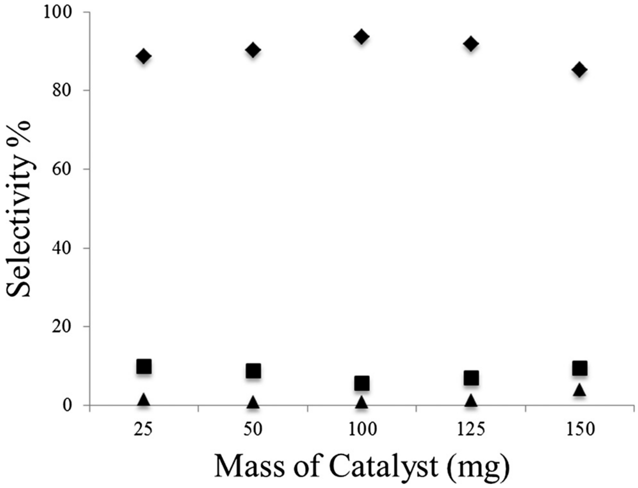

Fig. 6 Effect of catalyst mass on the selectivity of 2-MF from FA. Reaction conditions: substrate (1 g), $C_2H_4Cl_2$ (20 ml), autoclave reactor, 25 °C, 30 min, 1000 rpm, 3 bar. (▲) 2-Methytetrahydrolfuran, (♦) 2-methylfuran, (■) tetrahydrofurfuryl alcohol.

Effect of the catalyst amount. Increasing the amount of catalyst improved the overall catalytic performance, as shown in Fig. 5 and 6. The reaction was found to be very selective to 2-MF, when we used 100 to 125 mg 2.58 wt% Pd/TiO_2. The conversion kept increasing, but selectivity decreased slightly when 150 mg of catalyst was used. This can be attributed to side reactions due to the excess amount of catalyst. It confirms the very high selectivity observed using our Pd catalyst for the reduction of C=O to produce hydrocarbons, whereas the C=C reduction is almost inhibited even with the higher catalyst amounts. It suggests a different reaction pathway on the surface of the supported Pd catalysts, compared with the gas phase reduction of unsaturated hydrocarbons or aldehyde by using Pd catalysts.[47]

Effect of solvent. A comparison among different solvents was conducted and the results are shown in Table 3. Dichloroethane gives the best catalytic performance, and is very selective to 2-MF with very low production of tetrahydrofurfural alcohol. However, the reaction with octane shows very high activity but is not very selective for the formation of 2-MF. There are number of products which could not be identified properly. The GC-MS traces have indicated longer chain alcohols, and some dimers as well, and clearly the reaction was not very selective to 2-MF as is observed with 1,2-dichloroethane. Very limited reduction was observed when using acetonitrile and toluene as solvents. These observed solvent effect can be related with stability of the surface adsorbed H species generated from H_2 dissociation in presence of the solvents. Interaction between H_2 and H with the solvents could manipulate activity of the H species and then influence different reaction pathways.[48,49]

Table 4 MP-AES data of fresh and used catalysts

Theoretical loading	Fresh	Used
Pd (wt%)	Pd (wt%)	Pd (wt%)
1	0.50	0.51
2.5	1.26	1.36
5	2.58	2.5

Conclusions

We have demonstrated that FA can be converted selectively into 2-MF at room temperature using very low pressure of hydrogen with Pd supported catalysts. In this work highly active Pd catalysts with an abundance of very small particles (<2 nm) were prepared *via* a very simple impregnation method. By using these Pd catalysts, only O–H hydrogenated deoxygenation in furfuryl alcohol happened, C=C was very less reduced under these reaction conditions, wherein the only byproduct detected was tetrahydrofurfuryl alcohol <6%. The simpler preparation method and higher catalytic activity of the Pd catalysts suggests a great potential in this important area. The selective synthesis of 2-MF is a particularly attractive approach. The current study has reported a process which provides a possibility of synthesis of 2-MF, an important petroleum derivative using reaction conditions that minimise the consumption of energy in terms of heating and hydrogen, utilizing a very simple catalyst preparation method.

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Table 3 Effect of solvent on furfuryl alcohol hydrogenation[a]

		Selectivity (%)		
Solvents	Conversion (%)	2-Methylfuran	Tetrahydrofurfuryl alcohol	Unidentified products
Acetonitrile	14.9	100	0	0
Toluene	3.4	100	0	0
Octane	88.4	58.04	2.2	39.8
1,2-Dichloroethane	93.7	93.6	5.7	0

[a] Reaction conditions: substrate (1 g), 2.58% Pd/TiO_2 (0.1 g), solvent (20 ml), autoclave reactor, 25 °C, 30 min, 1000 rpm, 3 bar H_2.

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