

An Investigation of the Effect of the Addition of Tin to 5%Pd/TiO₂ for the Hydrogenation of Furfuryl Alcohol

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The selective hydrogenation of furfuryl alcohol was investigated at room temperature by using supported palladium catalysts. The catalysts are very selective to the formation of 2-methylfuran. Furthermore, the addition of tin to palladium showed similar catalytic activity, but was more selective to tetrahydrofurfuryl alcohol. Variation of the Sn/Pd ratio has shown

a considerable and interesting effect on the selectivity pattern. Addition of a small amount of Sn (1 wt%) shifted the selectivity towards tetrahydrofurfuryl alcohol and methyltetrahydrofuran, which are ring-saturated molecules. Increasing the tin ratio further decreased the catalytic activity and also showed very poor selectivity to either of these products.

Introduction

Furfuryl alcohol (FA) is an important bioderivative obtained from the hydrogenation of furfural, a product of xylose conversion.^[1] Selective hydrogenation and hydrogenolysis are considered to be the most effective methods for the conversion of furan compounds to valuable chemicals. There are studies that report the conversion of furfuryl alcohol into various fuel components, for example, 1,5-pentanediols,^[2] tetrahydrofurfuryl alcohol (THFA),^[3] and 2-methylfuran (2-MF).^[4] All of these components are important in terms of their application, but their synthesis under green reaction conditions represents a significant challenge.^[5] 2-MF is obtained from the hydrogenation of FA and furfural and is mainly used for the synthesis of crysanthemate pesticides, perfume intermediates and chloroquine lateral chains in medical applications.^[6] In 1931 copper chromite was the first catalyst reported for the conversion of FA in the liquid phase at 100 °C and 100–150 bar pressure of hydrogen.^[2] A yield of 70% pentanediol was observed under these reaction conditions. Subsequently, the synthesis of 2-MF was reported using Cr-based catalysts.^[5a] Nickel has been reported to be a selective catalyst for the synthesis of tetrahydrofurfuryl alcohol (THFA) from FA under very harsh reaction conditions (180 °C, 3.5 h).^[5c, 7] Ni^[4] and Cu^[6a] catalysts have been stated to be active catalysts for the selective hydrogenation of FA to 2-MF and furan. Pt, Pd and Ru catalysts supported on MnO^[5c] have been reported to be very efficient materials for the hydrogenation of FA at 120 °C, 30–60 bar H₂, for 4 h in the aqueous

phase. Pd-, Rh- and Pt-supported catalysts are observed to be less active compared with nickel, even at higher temperatures and pressures.^[7b, 8] All of these reports have shown the requirement for very harsh reaction conditions, both in terms of temperature and hydrogen pressure. Therefore, a process for the selective synthesis of 2-MF under green reaction conditions is desirable, but challenging, owing to the formation of various byproducts. We have recently reported that a 5 wt% Pd/TiO₂ catalyst can be used very effectively for the conversion of furfuryl alcohol into 2-methylfuran in 1,2-dichloroethane solvent at room temperature.^[9] Herein, we have compared the catalytic activity of the previously reported 5 wt% Pd/TiO₂ catalyst^[9] with a commercially available 5 wt% Pd/TiO₂ catalyst that can be used to benchmark our preparation method. Interestingly, there are differences in both the catalytic activity and the selectivity pattern for these two catalysts. These differences appear to be linked to the oxidation state of Pd in both catalysts. Furthermore, we have studied the addition of a second component, namely Sn, and observed similar catalytic activity, but more effective hydrogenation, with respect to double-bond saturation in the ring, which differs from the unmodified Pd/TiO₂ catalyst. In addition, we have also studied the effect of solvents, for example, methanol and ethanol, methanol was found to be a suitable alternative for 1,2-dichloroethane. The reaction was found to be less selective to 2-MF and a second product, THFA, was obtained when a Pd/Sn catalyst in 1:1 ratio was used. THFA is a low cost, biodegradable solvent with many agricultural and industrial applications. It can be prepared by the hydrogenation of furfural over Ni and Cu–Cr catalyst,^[2,3] however, severe environmental pollution can be created during the preparation and recycling of the Cu–Cr catalyst system^[5b] and a large amount of furfural condensates can be formed in this process. Ni, Pd, Ru and Rh, catalysts are commonly employed for the synthesis of THFA from furfuryl alcohol at temperatures above 50 °C using long reaction

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times.^[3,5c,8] 2-Methyltetrahydrofuran (MTHF), a completely saturated product and a very useful petroleum additive,^[10] has also been prepared in addition to THFA by varying hydrogen pressure (1–3 barg), with a Pd/Sn catalyst. Sn alloyed with other hydrogenation metals (e.g., Ru,^[11] Pt,^[12] Fe,^[13] Ni,^[14] Rh,^[15] and Pd^[16]) is known as an efficient catalyst for the hydrogenation of organic molecules over a long time period. Currently there are no reports of Sn/Pd catalysts for the hydrogenation of furan molecules. The aim of this research is to contribute an efficient green process with a novel catalyst composition for the conversion of furfuryl alcohol into useful organic molecules (2-MF, THFA and 2-MTHF) at very low temperature and pressure. We have also successfully substituted 1,2-dichloroethane as a solvent with methanol—a greener solvent for the conversion of bioderived molecules.^[17]

Results and Discussion

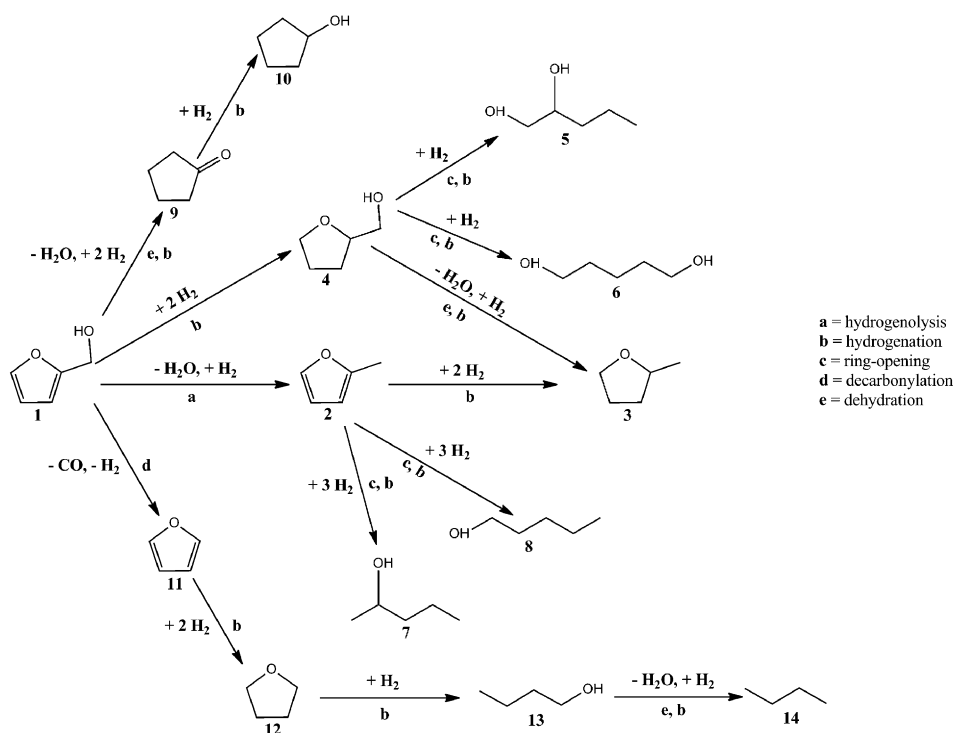
Initial experiments were carried out by using a commercially available 5%Pd/TiO₂ catalyst (denoted Std-5%Pd/TiO₂), which was used to provide a reliable benchmark for the catalysts designed for this study. An equivalent 5%Pd/TiO₂ (denoted IM-Pd/TiO₂) was prepared based on the impregnation methodology we have reported previously.^[9] These catalysts were investigated for the hydrogenolysis of furfuryl alcohol (1, Scheme 1) by using 1,2-dichloroethane as the solvent under mild conditions (25 °C and 3 barg H₂). Hydrogenation of the furan ring would give tetrahydrofurfuryl alcohol (4), hydrogenolysis of the molecule yields 2-methylfuran (2), which could ring open to give 2-pentanol (7), or ring hydrolysis of 2-methylfuran would give methyltetrahydrofuran (3). There are several possi-

	Reaction time [min]	Conversion [%]	Yield [%]	
			2-MF	2-pentanol
IM-Pd/TiO ₂	30	29	46	0
	60	76	91	2
	90	100	98	2
	120	100	85	15
	150	100	75	20
	180	100	65	25
Std-5%Pd/TiO ₂	30	22	35	0
	60	56	71	2
	90	77	82	5
	120	85	73	27
	150	87	79	25
	180	98	75	0

[a] Reaction conditions: 1,2-dichloroethane (15 mL), 3 barg H₂, catalyst (0.1 g), furfuryl alcohol (1 g) 25 °C.

ble products from furfuryl alcohol that are useful as fuel components; initially we focused on maximising the yield of 2-methylfuran. The comparison between Std-5%Pd/TiO₂ and IM-Pd/TiO₂ is shown in Table 1. It is clear that both of these catalysts are active for this reaction and both achieve complete, or close to complete, conversion of furfuryl alcohol after 180 min. IM-Pd/TiO₂ is, however, more active than Std-5%Pd/TiO₂, with a higher rate of initial activity and this catalyst reached 100% conversion of furfuryl alcohol after 90 min. Both catalysts produced high yields of 2-methylfuran, with IM-Pd/TiO₂ reaching a maximum yield of 98% after 90 min. The yield of 2-methylfuran then decreased as the yield of 2-pentanol increased, probably because of ring-opening hydrogenation. The Std-5%Pd/TiO₂ catalyst achieved a maximum yield of 2-methylfuran of 82%, and is clearly less active than the catalyst prepared by impregnation.

Powder X-ray diffraction (XRD) patterns of IM-Pd/TiO₂ and Std-5%Pd/TiO₂ are shown in Figure 1, with two clear differences between the samples. Firstly the Std-5%Pd/TiO₂ catalyst support is comprised solely of anatase TiO₂ (ICDD 01-070-7348), whereas IM-Pd/TiO₂ has a 4:1 anatase to rutile (ICDD 01-070-7347) ratio. TiO₂ composition is well known to have an effect on photocatalytic performance, but could also have an effect on the nature of the supported metal catalysts.^[18] The second observation is that although discernable



Scheme 1. Reaction pathways for the hydrogenation of furfuryl alcohol.

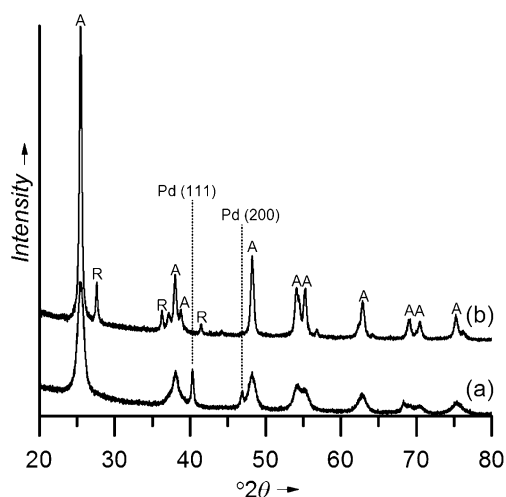


Figure 1. XRD patterns of a) Std-5%Pd/TiO₂ and b) IM-Pd/TiO₂. A denotes anatase phase, R denotes rutile phase and Pd highlights cubic metallic reflections.

reflections associated with the cubic Pd unit cell (ICDD 03-065-2867) are observed in Std-5%Pd/TiO₂, no reflections relating to any Pd phase are identifiable with IM-Pd/TiO₂. Microwave plasma atomic emission spectroscopy (MP-AES) analysis shows comparable Pd loadings for the Std-5%Pd/TiO₂ and IM-Pd/TiO₂ catalysts of 4.8 and 4.7%, respectively, therefore the lack of observable Pd reflections with IM-Pd/TiO₂ must be associated with the particles being below the detection limit of the XRD (ca. < 5 nm). The mean crystallite size of Pd was determined to be 22 nm (using Scherrer equation) in the Std-5%Pd/TiO₂ catalyst. This marked difference in mean Pd particles size can be related to the significant differing activity of the two catalysts, with smaller Pd crystallite size, as observed for IM-Pd/TiO₂, resulting in higher activity.

To probe the particle-size effect further, TEM analysis was performed on the samples. Representative images are shown in Figure 2. In agreement with the XRD results the TEM analysis

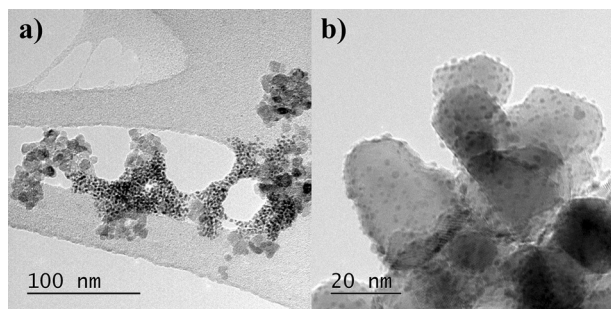


Figure 2. TEM images of a) Std-5%Pd/TiO₂ and b) IM-Pd/TiO₂.

highlighted significant differences between the two Pd catalysts. As can be seen in Figure 2a, the Std-5%Pd/TiO₂ catalyst seems to feature palladium clusters; it was not possible to carry out a reliable particle size distribution on these clusters owing to the overlap of the metal particles, but a tentative

measurement indicates that they are in the 2–3 nm range. The XRD analysis, however, suggests that significant agglomeration of the particles may be occurring within these clusters. In the IM-Pd/TiO₂ catalyst there is also some evidence of cluster formation, however, the metal particles are more evenly distributed as shown in Figure 2b. The particle size distribution is shown in Figure 3. The metal particles exhibit an average size

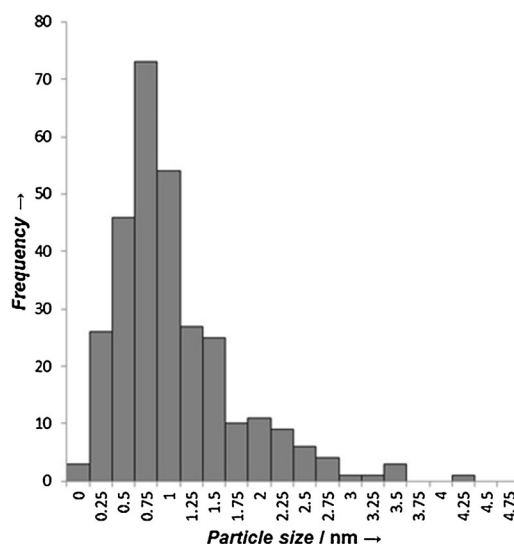


Figure 3. The particle size distribution (based on 300 particles) for IM-Pd/TiO₂.

of 1.18 nm and standard deviation of 0.67. The difference in the distribution of the palladium particle size in the two catalysts seems to provide a rational explanation for the difference in activity.

Comparison by XPS analysis of the IM-Pd/TiO₂ and Std-5%Pd/TiO₂ catalysts (Figure 4 and Table 2) reveals a significant difference in the initial Pd species present (Figure 5). The Std-5%Pd/TiO₂ sample has three distinct Pd environments, specifi-

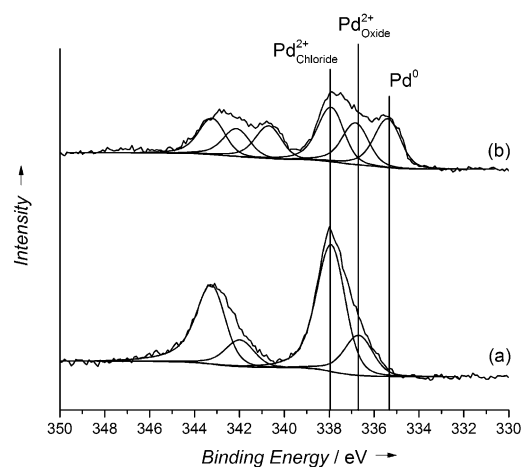


Figure 4. XPS curve-fitted Pd (3d) core-level spectra for 5% Pd/TiO₂ catalysts. a) IM-Pd/TiO₂ and b) Std-5%Pd/TiO₂.

Table 2. Quantified XPS results for the various Pd and Pd–Sn catalysts.

Sample	Assignment	Conc. [% At.]	Ratio					
			Ti/O	Pd/Sn	Sn/Pd	Pd/Ti	Sn/Ti	Pd/PdO/PdCl ^[a]
IM-Pd/TiO ₂	Pd 3d	3.59	0.37			0.14	0.07	0:1:3.25
	O 1s	67.56						
	Ti 2p	24.82						
	Cl 2p	4.03						
Std-5%Pd/TiO ₂	Pd 3d	1.48	0.42			0.05	0.04	1:0.85:1.11
	O 1s	67.66						
	Ti 2p	28.59						
	Cl 2p	2.27						
2.5:2.5 SnPd/TiO ₂	Pd 3d	1.58	0.42	0.83	1.21	0.06	0.07	1:4.09:0
	O 1s	67.05						
	Sn 3d 5/2	1.91						
	Ti 2p	28.2						
	Cl 2p	1.26						
1:4 SnPd/TiO ₂	Pd 3d	1.14	0.43	0.90	1.11	0.04	0.04	1:3.07:0
	O 1s	67.87						
	Sn 3d 5/2	1.26						
	Ti 2p	29.04						
	Cl 2p	0.68						
4:1 SnPd/TiO ₂	Pd 3d	0.33	0.44	0.17	5.82	0.01	0.06	1:1.42:0
	O 1s	67.79						
	Sn 3d 5/2	1.92						
	Ti 2p	29.57						
	Cl 2p	0.38						

[a] assignment based on binding energy of Pd, 335.5 eV; PdO, 336.8 eV and PdCl, 337.9 eV.

lyst under the reaction conditions we already established for the IM-5%Pd/TiO₂ catalyst (Table 3). We selected 60 min as an appropriate reaction time as neither of the catalysts had reached 100% conversion at this time, making differences in the activity apparent. The conversion of the furfuryl alcohol is higher than either of the Pd monometallic catalysts after the same reaction time, the yield of 2-methylfuran was, however, lower. A small amount of methyltetrahydrofuran was also detected when using these catalysts, resulting from a sequential hydrogenolysis, hydrogenation reaction (Scheme 1) the ring-opening product 2-pentanol was not detected. To increase the yield of methyltetrahydrofuran the temperature of the reaction was increased to 50 °C, which led to a slight increase in the conversion of furfuryl alcohol. At this temperature, methyltetrahydro-

cally Pd⁰ (335.5 eV) and Pd²⁺ present as both oxide (336.8 eV) and chloride (337.9 eV). IM-Pd/TiO₂ comprises exclusively Pd²⁺, with chloride being the majority species. Correlations between catalyst selectivity and Pd oxidation state are, therefore, possible because the Std-5%Pd/TiO₂ catalyst comprises some Pd metal and this is less selective towards 2-methylfuran. The activation of ring-opening pathways can be attributed to the presence of metallic Pd, and consequently, the MF yield is decreased. Both catalysts show increased 2-pentanol yields over longer times, therefore, it can be rationalised that under the reducing reaction conditions the oxidized Pd species present in both catalysts are reduced to metallic Pd. XPS analysis of the used catalysts confirms this, as expected, under reducing reaction conditions, there is significant amounts of Pd⁰ in both catalysts (Pd/Pd–O/Pd–Cl = 1:0.92:0.8 and 1:0.71:0.81 for IM-Pd/TiO₂ and Std-5%Pd/TiO₂, respectively), which correlates to the observed increase in 2-pentanol formation from the ring-opening pathway. The Pd/Ti ratio suggests the Pd dispersion for the monometallic catalyst prepared by impregnation is greater than the Std-5%Pd/TiO₂ catalyst, which correlates with the XRD Pd particle sizes and TEM data and further suggests the improved initial activity rates are a consequence of this improved Pd dispersion.

It has been reported that Sn–Pd bimetallic catalysts are active for hydrogenation and hydrogenolysis reactions,^[10] therefore, we synthesized a 2.5 wt%Pd–2.5 wt%Sn/TiO₂ catalyst by impregnation methodology and investigated this cata-

Table 3. Catalytic hydrogenolysis of furfuryl alcohol with SnPd/TiO₂ (2.5:2.5 wt %).^[a]

T [°C]	Conversion [%]	Yield [%]	
		2-MF	MTHF
25	86.5	57.4	1.3
50	93.6	77.2	0
80	80.8	53.4	0

[a] Reaction conditions: 1,2-dichloroethane (15 mL), 1 barg H₂, catalyst (0.1 g), furfuryl alcohol (1 g), 60 min.

furan was no longer detected and the yield of 2-methylfuran was increased and was slightly higher than the monometallic Pd catalyst after the same reaction time. In an effort to achieve more control of the product selectivity, we studied the bimetallic catalyst at various pressures of hydrogen, the results of these reactions are shown in Table 4.

Increasing the pressure of hydrogen did not seem to have a pronounced effect on the conversion, suggesting that the hydrogen is not mass-transfer limited under our conditions. We did observe slight differences in the yields of 2-methylfuran and methyltetrahydrofuran at the different pressures, but it seems likely that this is related to the conversion rather than an alternate reaction pathway operating at different pressures.

As dichloromethane is not a particularly favorable solvent, with respect to green chemistry, we repeated the reaction

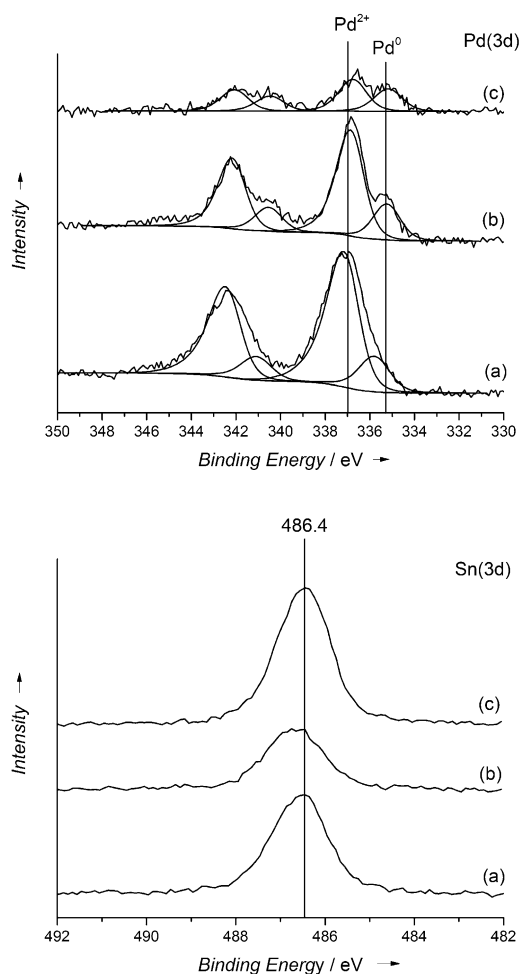


Figure 5. XPS Pd(3d) and Sn(3d) spectra for the 5 wt % xSn/yPd/TiO₂ samples. a) 2.5Sn/2.5Pd, b) 1Sn/4Pd and c) 4Sn/1Pd.

Pressure [barg]	Conversion [%]	Yield [%]	2-MF	MTHF
1	86.5	57.4	1.3	
2	100	44	1.62	
3	95	50	1	

[a] Reaction conditions: 1,2-dichloroethane (15 mL), catalyst (0.1 g), furfuryl alcohol (1 g), 25 °C, 60 min.

using the bimetallic catalyst prepared by using impregnation methodology with methanol and ethanol as solvents. Again, the change of solvent did not make a significant difference to the conversion of the furfuryl alcohol (Table 5), although the highest conversion was observed with methanol. The significant difference, however, was in terms of the product distribution, the use of either methanol or ethanol as a solvent led to a significantly increased yield of tetrahydrofurfuryl alcohol. High selectivity towards tetrahydrofurfuryl alcohol represents a different reaction pathway (Scheme 1) because this requires

Solvent	Conversion [%]	Yield [%]		
		2-MF	MTHF	THFA
ethanol	92	50	3	43
methanol	100	25	8	52
1,2-dichloroethane	86.5	57.4	1.3	–

[a] Reaction conditions: 1 barg H₂, catalyst (0.1 g), furfuryl alcohol (1 g), 25 °C, 60 min.

the selective hydrogenation of the furan double bonds with hydrogenolysis of the alcohol. Changing the selectivity of a reaction by the choice of solvent is an effect we have previously reported in the case of oxidation reactions.^[19]

The Pd monometallic IM-5%Pd/TiO₂ catalyst displayed the best yield of 2-methylfuran and the bimetallic catalyst displayed the highest yield of tetrahydrofurfuryl alcohol with methanol as the solvent. Consequently, we synthesised bimetallic catalysts with different ratios of Sn and Pd. We have previously reported that changing the ratio of metals in a bimetallic catalyst can have a significant effect on the activity and selectivity in benzyl alcohol oxidation.^[20] For completeness we also tested the IM-Pd/TiO₂ catalyst under these conditions. As with the bimetallic catalysts, the conversion of the IM-Pd/TiO₂ is higher than when 1,2-dichloromethane is used as the solvent. The selectivity towards 2-MF was significantly lower, confirming that solvent can make a significant difference to the product selectivity, an effect we have previously observed.^[19] Using methanol as the solvent with the bimetallic catalysts we observed that the more-palladium-rich catalyst (Sn/Pd=1:4) forms mostly tetrahydrofurfuryl alcohol, the yield of tetrahydrofurfuryl alcohol is the same as that for the Sn/Pd=1:1 catalyst, however, these catalysts differ in their selectivity towards other products, as shown in Table 5. When the metals are present in a 1:1 ratio in the catalyst there is a significant amount of 2-methylfuran, however, when the metal component of the catalyst is mainly Pd the 2-methylfuran product is not observed and the sequential product, methyltetrahydrofuran, is observed. This is in agreement with the data reported on the Pd monometallic catalyst, as this was the most active of all the catalysts we present in this study. The small amount of Sn may prevent the ring-opening pathway previously observed, allowing for the hydrogenation reaction to take place. The Sn-rich catalyst (Sn/Pd=4:1) gave a lower yield of tetrahydrofurfuryl alcohol, however, methyltetrahydrofuran was not observed. When using this catalyst, the hydrogenolysis pathway is in operation because 2-methylfuran is observed.

We have investigated the catalysts by using X-ray photoelectron spectroscopy. Figure 5 shows the Pd(3d) and Sn(3d) core-levels, determined by XPS, for the Sn–Pd bimetallic catalysts with varying ratios of Sn/Pd. At this point it is worth noting that the Sn core level does not typically shift between 2+ and 4+ states, however, application of the modified Auger parameter (919.2 eV) indicates that Sn is present as SnO₂. This is in agreement with XRD analysis (Figure 6c), which shows the sys-

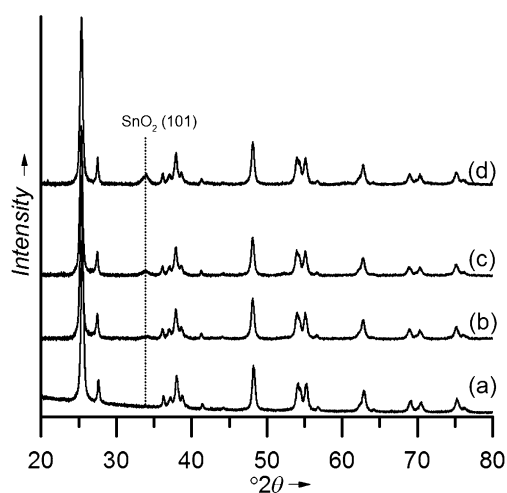


Figure 6. XRD patterns of Pd/TiO₂ and SnPd/TiO₂. a) 5% Pd/TiO₂, b) 1:4 SnPd/TiO₂, c) 2.5:2.5 SnPd/TiO₂ and d) 4:1 SnPd/TiO₂.

tematic growth of a reflection at $2\theta = 33.9^\circ$, which correlates with the (101) SnO₂ plane, with increasing Sn content. We note that no Pd reflections are observable for any of the Sn/Pd catalysts. TEM images of the Sn/Pd catalysts are shown in Figure 7. There are small ($\approx 2\text{--}3\text{ nm}$) particles observed on all

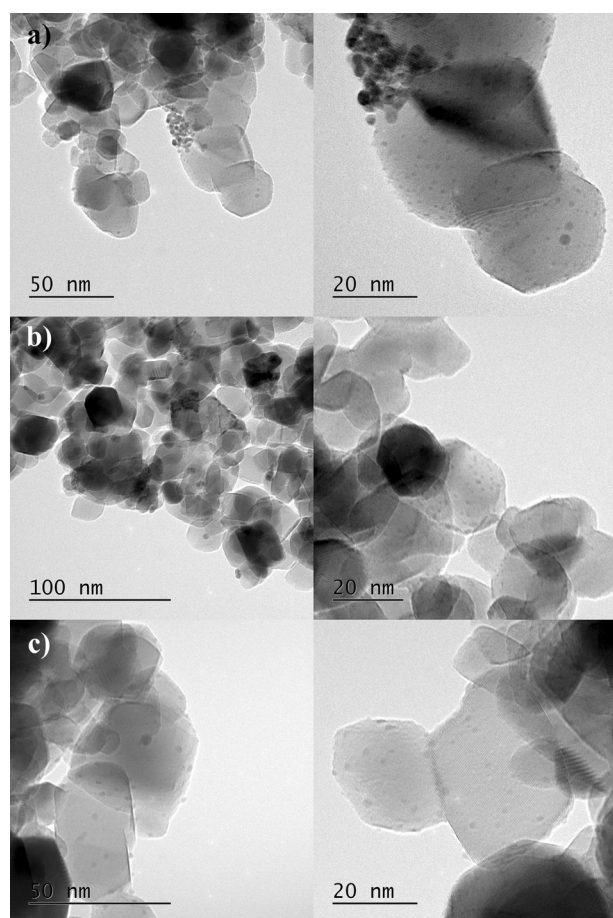


Figure 7. TEM images of a) 1:1 SnPd/TiO₂, b) 1:4 SnPd/TiO₂ and c) 4:1 SnPd/TiO₂.

three catalysts; however, at higher magnification, smaller ($\approx 0.5\text{ nm}$) particles are also observed. Bimodal particle size distributions have been previously reported for catalysts prepared by impregnation.^[21] However, owing to the size of the particles we were unable to perform a statistically significant particle size distribution because the small particles are at the detection limit for this technique. XPS analysis showed that the Pd is predominantly PdO (337 eV) for all Sn/Pd ratios, with some metallic Pd (335.5 eV), but no Pd chloride species was present (Table 2), as observed in the monometallic Pd/TiO₂ catalyst. Varying the metal ratio was found to effect the relative concentrations of the Pd species present (Table 6); for 4:1

Table 6. Variation of metal loading for catalytic hydrogenolysis of furfuryl alcohol.^[a]

Catalyst/TiO ₂	Conversion [%]	Yield [%]		
		2-MF	MTHF	THFA
IM-5%Pd	81.7	14.3	1.5	69.4
Sn/Pd = 4:1	75	12	0	23
Sn/Pd = 1:4	85	0	25	52
Sn/Pd = 2.5:2.5	100	25	8	52

[a] Reaction conditions: methanol, 1 barg H₂, catalyst (0.1 g), furfuryl alcohol (1 g), 25 °C, 60 min.

SnPd/TiO₂ Pd²⁺ dominates, whereas for lower Pd concentrations the Pd⁰ component becomes more significant. Interestingly, for 2.5:2.5 SnPd/TiO₂ and 1:4 SnPd/TiO₂ there is no significant difference in the Pd/Sn ratio observed by XPS (0.83 and 0.90, respectively). This suggests that a significant amount of Pd within the 2.5:2.5 SnPd/TiO₂ is occluded within the SnO₂. For the diluted Pd system, this ratio understandably decreases to 0.17 and suggests a poor dispersion of the Pd on the Sn, and could explain the different reaction pathway observed because the required Pd site is hindered with respect to access by the reactants.

Conclusions

We have demonstrated that furfuryl alcohol can be converted selectively into 2-methylfuran at room temperature by using very low pressure of hydrogen with Pd-supported catalysts. Highly active supported Pd catalysts were prepared by using an impregnation method. By using these Pd catalysts, only O–H hydrogenated deoxygenation occurred, C=C reduction was observed only to a limited extent under these reaction conditions. Furthermore, we have shown that by the correct choice of metal, supported on TiO₂, we can drive the reaction towards particular reaction pathways, with catalyst tuning we can reduce the amount of ring hydrogenation that occurs, switch off the ring opening reactions or drive the ring hydrogenation forward so that no hydrogenolysis products are observed. Pd/TiO₂ catalysts favour the hydrogenolysis of furfuryl alcohol to 2-methylfuran, followed by the sequential ring opening to form 2-pentanol. The addition of Sn switched off ring opening

and facilitated the hydrogenation of 2-methylfuran to 2-methyltetrahydrofuran, which is a completely saturated molecule and is an important petroleum additive.^[10] The improved selectivity of IM-Pd/TiO₂ was attributed to the absence of metallic Pd, as observed by XPS analysis. We have also shown that the reactions of furfuryl alcohol can be performed under mild, green conditions, with favorable reactions occurring at low pressure, low temperature and by using the relatively environmentally benign solvents, methanol and ethanol.

Experimental Section

Materials

Furfuryl alcohol (98%), 1,2-dichloroethane (98%), methanol (99.8%), ethanol (99.8%) and all reaction intermediates were purchased from Sigma–Aldrich and used as received. Palladium(II) chloride and tin(II) chloride metal precursors were also purchased from Sigma–Aldrich. Titania was purchased from Degussa. Pure hydrogen (99.9%) and nitrogen (99.9%) were obtained from BOC. Std-5% Pd/TiO₂ was purchased from Johnson Matthey (product code 11002).

Wet impregnation method

All monometallic catalysts supported on titania were produced by using the standard wet impregnation method, whereby PdCl₂ was added to deionised water (2 mL) and stirred for approximately 15 min at 80 °C until the Pd dissolved completely. TiO₂ support was added to the solution and stirred to form a paste. The paste was subsequently dried at 110 °C for 16 h, before being ground in a pestle and mortar, transferred to a 4 inch ceramic combustion boat, and calcined in static air (400 °C, 3 h, 20 °C min⁻¹). Bimetallic catalysts were prepared in the same manner, with the concomitant heating and stirring of the PdCl₂ and SnCl₂ precursors.

Analysis

Powder XRD was carried out by using a PANalytical X'Pert Pro with a Cu_{Kα} 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.

Microwave Plasma Atomic Emission Spectroscopy (MP-AES) was performed by using a Agilent 4100 MP-AES. The Pd content was analysed with two emission lines with 340 and 363 nm used for Pd. The samples were introduced to the nitrogen plasma by using a single-pass spray chamber at a pressure of 120 kPa without air injection. The instrument was calibrated with 10, 20, 40, 50 ppm standards in 10% aqua regia along with a 10% aqua regia blank. The samples were tested 3 times and the average result was used. A 10% aqua regia rinse solution was introduced between samples for 15 s to ensure there was no sample contamination.

X-ray photoelectron spectroscopy (XPS) samples were characterized by using a Kratos Axis Ultra-DLD photoelectron spectrometer, using monochromatic Al_{Kα} 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.

Transmission electron microscopy (TEM) was carried out by using a Jeol 2100 with a LaB6 filament operating at 2000 kV. Samples were prepared by dispersing the powder catalyst in ethanol and dropping the suspension onto a lacey carbon film over a 300 mesh copper grid.

Furfuryl alcohol hydrogenation

A Colaver glass reactor was charged with furfuryl alcohol (1.0 g), solvent (15 mL) and catalyst (0.1 g). The reactor was sealed, pressurised with 3 bar nitrogen, and purged three times before being pressurised with hydrogen (1–3 bar constant pressure), and stirred (1000 rpm) for 60 min unless otherwise specified. The post-reaction mixture was centrifuged prior to being analysed by GC (Bruker Sion 456-GC fitted with a Br-1 ms capillary 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, with 1-propanol being the external standard.

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