Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

The influence of metal selection on catalyst activity for the liquid phase hydrogenation of furfural to furfuryl alcohol

Á. O'Driscoll[a,b,*], J.J. Leahy[a,b], T. Curtin[a,b]

[a] Carbolea Research Group, Department of Chemical and Environmental Sciences, University of Limerick, Limerick, Ireland
[b] Materials and Surface Science Institute (MSSI), University of Limerick, Limerick, Ireland

ARTICLE INFO

Article history:
Received 14 December 2015
Received in revised form 2 June 2016
Accepted 4 June 2016
Available online xxx

Keywords:
Furfural
Furfuryl alcohol
Platinum catalyst
Surface organometallic catalysis
Liquid phase hydrogenation
Biomass

ABSTRACT

In this work the replacement of toxic chromium containing catalysts for the selective hydrogenation of furfural to furfuryl alcohol was investigated. The initial focus was on the synthesis of monometallic catalysts by wet impregnation and concentrated on the employment of metals such as platinum, palladium, copper and nickel. Experiments were conducted using ethanol as the solvent which was found to have a negative effect on the selectivity to the desired product, furfuryl alcohol, with high quantities of 2-Furaldehyde diethyl acetal and difurfuryl ether formed. Consequently, toluene was selected as an alternative solvent facilitating selectivity to furfuryl alcohol only. It was found that platinum was the most promising metal of those studied as it displayed higher selectivity to furfuryl alcohol and was subsequently employed for the synthesis of bimetallic catalysts. The bimetallic catalysts were synthesised by surface reactions using a variety of promoter metals selected according on their electronegativity. It was found that, while the selectivity of all catalysts to furfuryl alcohol was close to 100%, the conversion was influenced significantly by the second metal and followed the order tin > molybdenum > manganese > barium > iron > nickel. The purpose of the research was to produce an active catalyst for the liquid phase hydrogenation under suitable industrial conditions with the results presented here conducted at 100 °C and 20 bar hydrogen pressure. Furfural conversion of 47% and close to 100% selectivity to furfuryl alcohol was achieved using a 0.6%Pt0.4%Sn/SiO_2 catalyst.

1. Introduction

Research to develop alternative liquid transport fuels has increased considerably in recent years influenced by the implementation of legislation and directives on alternative energy which sets targets for transposing members. Europe has set targets such as the Renewable Energy Directive to make renewable energy sources account for 20% of overall energy and 10% of transport energy by 2020 [1]. To achieve these targets in an ethical, environmentally sustainable and economical manner the use of lignocellulosic biomass or agri-waste for the production of second generation biofuels is proposed [2]. The production of biofuels from hemicellulose requires acid hydrolysis to open the biomass structure giving large quantities of xylose [3]. The synthesis of furfural (FF) as a by-product of this biofuel production process has developed an additional important research area.

Furfural, produced by the acid-catalysed dehydration or hydrolysis of xylose, is a versatile and renewable chemical with wide industrial applications [4–6]. These include uses in the agrochemical, fragrance and plastics industries while it is also a building block for the synthesis of various other chemicals and chemical products including nylons and adhesives [5,7,8]. The hydrogenation of furfural to furfuryl alcohol (FA) is a single step process and the most popular application of furfural conversion with approximately 60–62% of the furfural produced worldwide converted to furfuryl alcohol [9].

Furfuryl alcohol is formed from a simple hydrogenation reaction in the presence of a catalyst. The C=O of the aldehyde functional group in furfural breaks while the addition of hydrogen to the oxygen results in an alcohol group (O—H) with an additional hydrogen bonded to the exocyclic carbon of the furan based structure giving furfuryl alcohol. Furfuryl alcohol is used mainly in the polymer industry together with the production of synthetic fibres, rubbers, resins and farm chemicals. It is used in the manufacture of lysine, vitamin C and lubricants, the production of foundry sand binders in the metal casting industry and as a chemical building block for

---

* Corresponding author at: Carbolea Research Group, Department of Chemical and Environmental Sciences, University of Limerick, Limerick, Ireland.
E-mail address: aine.odriscoll@ul.ie (Á. O'Driscoll).

http://dx.doi.org/10.1016/j.cattod.2016.06.013
0920-5861/© 2016 Elsevier B.V. All rights reserved.

Please cite this article in press as: Á. O'Driscoll, et al., The influence of metal selection on catalyst activity for the liquid phase hydrogenation of furfural to furfuryl alcohol, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.06.013

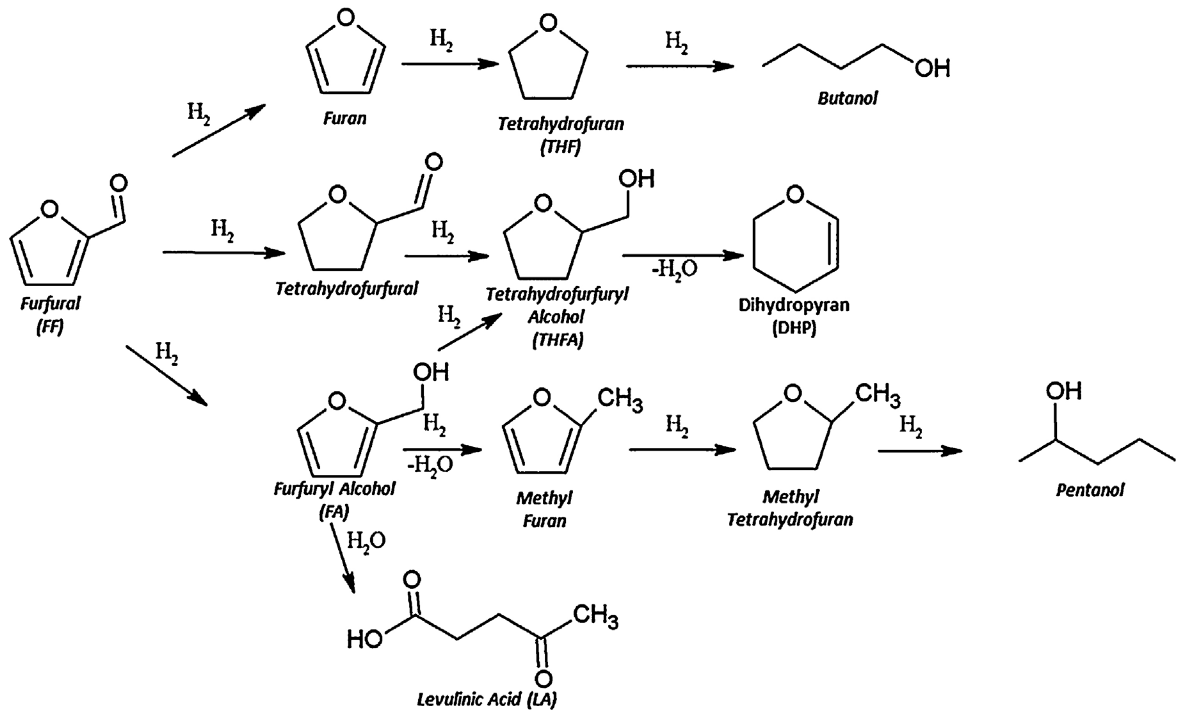

Fig. 1. The hydrogenation pathway of the platform chemical, furfural.

drug synthesis. Furfuryl alcohol is also used in the production of other products in the fine chemical industry [10–13].

The derivatives of furfural, some of which are outlined in Fig. 1, include furfuryl alcohol, tetrahydrofuran, 2-methylfuran, furoic acid, hydroxymethylfurfural, furylidene, furan and resins [14–17]. Many of these products are formed via furfural hydrogenation with a variety of additional reactions including furfural decarbonylation and oxidation also possible. It is therefore of great importance to choose a catalyst which is selective to the desired reaction route.

The industrial catalyst for the hydrogenation of furfural to furfuryl alcohol is copper chromite and is well known to be environmentally toxic, promoting extensive research to develop suitable alternatives [18]. The necessity to produce an alternative has increased the interest in heterogeneous catalysts for the synthesis of fine chemicals.

A wide variety of chromium free catalysts exist in literature employing an extensive selection of support and metal combinations. Catalysts investigated for liquid phase research were examined as a basis for metal selections applied in this work. Metals frequently selected include copper [19–22] and nickel [23–26] while metals such as platinum [27–29] and palladium [30–32] are sparsely reported with publications limited to dedicated research groups. Overall, no trends between metal selection and catalyst activity are evident from the literature although bimetallic catalysts are generally more active than monometallic catalysts for the desired reaction.

Furfural may be hydrogenated to furfuryl alcohol in the liquid or gas phase with the industrial process utilising high temperature and pressure although the chromium containing catalyst used in industry achieves only moderate activity for this reaction [29,33,34]. Vapour phase is often favoured over liquid phase due to the uneconomic outcome of large-scale batch processes. However, vapour phase also has issues relating to the production of undesired derivatives at high furfural conversion together with deactivation of the catalyst [35]. A wide variety of catalyst synthesis techniques have been investigated for this reaction from techniques such as impregnation [30,34] and co-precipitation [19,26] to complex techniques including surface reactions together with synthesising supported and encapsulated metal nanoparticle catalysts [29,36–38].

This work focuses on the synthesis of a catalyst that is active for the hydrogenation of furfural to furfuryl alcohol. The selectivity to furfuryl alcohol is crucial which is the emphasis for the selection of the primary metal. An analytical approach regarding the electronegativity of metals is applied to the selection of a second metal in order to increase furfural conversion. The solvent used for the reaction is also scrutinised to ensure the selection does not have a negative effect on the desired reaction.

2. Materials and methods

Furfural, furfuryl alcohol, ethanol, toluene, hydrofluoric acid, hexanol, 1-propanol and *n*-heptane, all of analytical reagent quality, were obtained from Sigma-Aldrich. Metal salts for catalyst preparation; copper (II) nitrate hydrate, nickel (II) nitrate hexahydrate, platinum (II) acetylacetonate, tetraaminepalladium (II) chloride monohydrate, tetrabutyl tin, iron (II) chloride tetrahydrate, manganese (II) acetate tetrahydrate, nickel (II) nitrate heptahydrate, barium acetate molybdenum acetate together with lanthanum (III) chloride heptahydrate, aluminium isopropoxide, pleuronic® P-123 (P123) and tetraethyl orthosilicate (TEOS) were also obtained from Sigma-Aldrich. Metal standards were obtained from Lennox Dublin. Commercial palladium catalysts and catalyst supports, SiO_2 and TiO_2 were obtained from Sigma-Aldrich while ß-Zeolite was obtained from Zeolyst International.

3. Experimental

3.1. Catalyst preparation

All monometallic catalysts were produced using wet impregnation. The required amount of a precursor salt was added to 50 ml of ethanol followed by the addition of the support. The suspen-

Please cite this article in press as: Á. O'Driscoll, et al., The influence of metal selection on catalyst activity for the liquid phase hydrogenation of furfural to furfuryl alcohol, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.06.013

Table 1

Catalysts tested for furfural conversion and furfuryl alcohol selectivity. (Reaction conditions: 1 g catalyst, 25 ml FF, 175 ml solvent (ethanol), P_{H2} = 20 bar, T = 100 °C, t = 300 min).

Catalyst	Expected Metal Loading (%)	Measured Metal Loading (%)	Conversion of Furfural (%)	Selectivity to Furfuryl Alcohol (%)
Cu/SiO_2	1	1.1	29	<1
Ni/SiO_2	1	0.9	37	<1
Pd/SiO_2	1	1.0	44	10
Pt/SiO_2	1	0.6	31	29
Cu/SiO_2	2	2.0	27	<1
Ni/SiO_2	2	1.9	29	5
Pd/SiO_2	2	1.9	45	8
Pt/SiO_2	2	1.4	41	35

sion was stirred for 16 h at room temperature, followed by solvent evaporation and calcination in air at 450 °C for 300 min.

The catalyst support Al-SBA-15 was synthesized according to a procedure reported by Srivastava et al. [39].

Surface reactions were used for the production of bimetallic catalysts. A calcined platinum catalyst, produced by wet impregnation, was placed in an autoclave (Parr 4560) and reduced at 300 °C for four hours at 20 bar hydrogen pressure. A solution was prepared containing the required amount of the desired metal precursor dissolved in 200 ml of solvent selected depending on the solubility of the salt. Iron, molybdenum, manganese and nickel salts were dissolved in 1-Propanol with tin and barium salts dissolved in *n*-heptane and deionised water respectively. This solution was degassed using nitrogen and added to the reactor and stirred at 600 rpm for four hours at 90 °C and 20 bar hydrogen pressure. This suspension was then filtered and dried overnight at 60 °C.

3.2. Catalytic tests

The liquid phase hydrogenation of furfural was carried out in a 600 ml autoclave (Parr 4560) equipped with a mechanical stirrer. For a typical experiment, 1.0 g of catalyst was placed in the reactor and reduced at 300 °C and 20 bar of hydrogen pressure for 4 h. The reactor was then flushed with nitrogen and charged with 25 ml of furfural and 175 ml solvent. The reactor was heated to 100 °C and the pressure was rapidly increased to 20 bar hydrogen with a stirring speed of 600 rpm. Homogeneous mixing was assumed and samples were taken at regular intervals for analysis by gas chromatography (Agilent Technologies 7820A) equipped with an FID detector. A Restek Stabilwax® 10623 30 m × 0.25 mm × 0.25 μm column was used, with nitrogen as the carrier gas at a flow rate of 12 ml min^{-1} and a split ratio of 1:25. The injector and detector were operated at 300 °C and 250 °C, respectively. A selection of samples were analysed using gas chromatography-mass spectroscopy (Agilent Technologies 7890A) under the same conditions for product identification purposes.

3.3. Formulae

The conversion of furfural, selectivity to furfuryl alcohol and reaction yield were calculated as follows;

$$\text{FFConversion}\,(\%): \frac{n_{FF}^{o} - n_{FF}^{S}}{n_{FF}^{o}} \times \frac{100}{1}$$

$$\text{FASelectivity}\,(\%): \frac{n_{FA}}{n_{FF}^{o} - n_{FF}^{S}} \times \frac{100}{1}$$

$$\text{Yield}\,(\%): \frac{n_{FA}}{n_{FF}^{o}} \times \frac{100}{1}$$

n_{FF}^{o} = initial moles of furfural

n_{FF}^{s} = moles *of* furfural in sample

n_{FA} = moles of furfuryl alcohol

3.4. Catalyst characterisation

The catalysts were characterised by Atomic Absorption Spectroscopy (AAS). Prior to AA analysis, digestion was performed using an Anton Parr 8NXF100 autoclave where 25.0 mg catalyst was added to 10 ml hydrochloric acid. The sample was digested with a thermal input of 900 W using a three step method including 15 min ramp, 60 min hold and 30 min cooling. Lanthanum chloride was added to the digested sample to eliminate interferences from hydrochloric acid. A Varian Spectra 220 Atomic Absorption Spectrometer was used to analyse the samples. For analysis of platinum catalysts an acetylene air flame and a platinum hollow cathode lamps were used at a wavelength of 265.9 nm with a slit width of 0.2 nm.

Scanning electron microscopy (SEM) & energy-dispersive X-ray analysis (EDAX) were also used for measurement of metal content using a Hitachi SU-70 SEM operating at 20 kV equipped with an EDAX detector. Samples were placed directly onto carbon tape on the specimen stub with no further pre-treatment performed.

Surface area analysis was used to establish surface area, pore volume and pore radius of the catalysts by nitrogen physisorption using a Quantachrome Autosorb AS-1. For each analysis, 10 mg of sample was outgassed under vacuum at 150 °C for 12 h to remove water and other atmospheric contaminants followed by analysis consisting of measurement of adsorption and desorption of nitrogen gas on the sample conducted at −196 °C.

4. Results and discussion

Initial catalyst testing focused on four selected metals, platinum, palladium, nickel and copper supported on silica for furfural conversion and selectivity to furfuryl alcohol. A complete list of the catalysts tested is outlined in Table 1 which summarises the hydrogenation performance of the prepared catalysts. Furfural conversion after 5 h reaction ranged from 27 to 45% indicating that all catalysts showed some activity for the reaction. The selectivities to furfuryl alcohol ranged from <1 to 35%. The overall low furfuryl alcohol selectivity was as a result of the production of undesirable products. The selectivity to the desired product was particularly low for the nickel and copper based catalysts. Although in general the catalyst activity was poor for the desired reaction, the apparent influence of each metal was clear with palladium and platinum indicating a positive influence on conversion and selectivity respectively. Therefore, these two metals were the focus of catalyst development which concentrated on increasing furfural conversion and furfuryl alcohol selectivity.

Please cite this article in press as: Á. O'Driscoll, et al., The influence of metal selection on catalyst activity for the liquid phase hydrogenation of furfural to furfuryl alcohol, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.06.013

Table 2
Palladium supported catalysts examined.

Palladium Supported Catalysts	Expected Metal Loading (%)	Actual Metal Loading (%)	Surface Area (m^2/g)
Pd/SiO_2	2.0	1.9	566
Pd/TiO_2	2.0	0.4	16
Pd/Al-SBA-15	2.0	0.9	538
Pd/ß-Zeolite	2.0	1.6	509
10%Pd/C-Sigma Aldrich	–	10.0[a]	950[b]
1%Pd/C-Sigma Aldrich	–	1.0[a]	760[b]

[a] Manufacturer Analysis.
[b] Characterisation by [40].

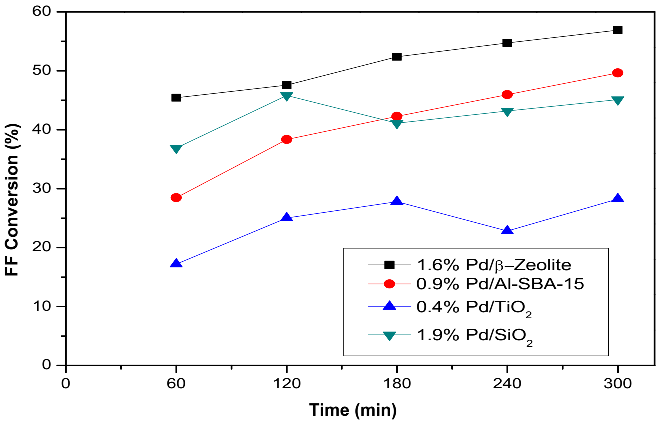

Fig. 2. The conversion of furfural using the indicated synthesised catalysts. (Reaction conditions: 1 g catalyst, 25 ml FF, 175 ml solvent (ethanol), P_{H_2} = 20 bar, T = 100 °C).

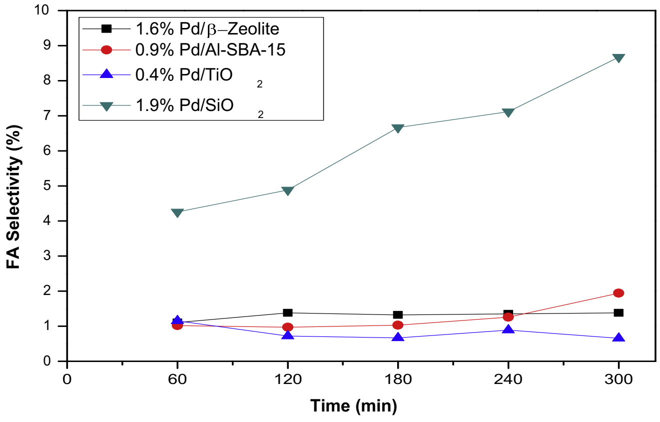

Fig. 3. Influence of the indicated catalysts on selectivity to furfuryl alcohol with reaction time. (Reaction conditions: 1 g catalyst, 25 ml FF, 175 ml solvent (ethanol), P_{H2} = 20 bar, T = 100 °C).

5. Palladium supported catalysts

From initial testing, palladium was observed to be the most influential metal for furfural conversion. Therefore, this catalyst was investigated further with the aim of increasing furfural conversion and improving furfuryl alcohol selectivity.

A selection of supports were chosen and used in the synthesis of a number of palladium catalysts. The supports chosen included Al-SBA-15, ß-Zeolite and TiO_2. All catalysts were prepared in a similar way (wet impregnation) with a view to investigation the role of support. The hydrogenation performance of the synthesised catalysts was compared to commercial palladium catalysts obtained from Sigma Aldrich. A complete list of these catalysts is shown in Table 2 which also presents the B.E.T surface areas of the synthesised and commercial catalysts. The expected palladium loading for the synthesised catalysts was 2 wt% and the table also includes the atomic absorption measured palladium loading for each of these prepared catalysts. The highest surface area was exhibited by the commercial catalysts from Sigma-Aldrich, 1%Pd/C and 10%Pd/C, which used activated carbon as the support. The synthesised catalysts based on SiO_2, Al-SBA-15 and ß-Zeolite had comparable surface areas however TiO_2 displayed a much lower surface area.

The hydrogenation results for furfural conversion using the synthesised catalysts 1.9%Pd/SiO_2, 0.4%Pd/TiO_2, 0.9%Pd/Al-SBA-15 and 1.6%Pd/ß-Zeolite are presented in Fig. 2. A difference in furfural conversion was seen for the selection of supports studied indicating that the supports may influence the conversion. This is most notable when 1.9%Pd/SiO_2 and 1.6%Pd/ß-Zeolite are compared as they have similar surface areas but despite the ß-Zeolite having a lower palladium content it displays higher furfural conversion. There are many factors which may influence the catalyst activity including the acidity of the support, the interaction between the metal and the support, the surface area and the metal content. It was observed that low conversion occurred when surface area and metal content were also low.

Fig. 3 shows the selectivity to furfuryl alcohol with hydrogenation time for the prepared catalysts. Overall, the selectivity was poor however it seems that selectivity to furfuryl alcohol was promoted by using silica as a support. The furfural conversion and furfuryl alcohol selectivity results may indicate the importance of the acidity of the supports on the overall catalyst activity. The presence of aluminium in the beta zeolite and the Al-SBA-15 makes these supports acidic in nature and both of these catalysts presented the highest furfural conversions. However, although these acidic supports resulted in the promotion of furfural conversion they presented low furfuryl alcohol selectivity. This may be a result of furfural acetalization which is a non-catalytic reaction facilitating the conversion of furfural due to the presence of ethanol. Alternatively, the low furfuryl alcohol selectivity may be due to etherification with ethanol as the Brønsted acid supports can influence the direction of the reaction while Lewis acid supports such as TiO_2 facilitate furfuryl alcohol etherification via the Meerwein-Pondorf-Verley reaction whereby the carbonyl group and the alcohol coordinate to a Lewis acid metal centre and a hydride transfer from the alcohol to the carbonyl occurs [41–44].

TEM analysis was performed on the synthesised palladium catalysts. Overall, the dispersion of the metal particles was similar for all catalysts (Supplementary Information, Fig. A1–4) with metal particles of 2–5 nm present on all supports with the exception of 0.4%Pd/TiO_2, most likely due to the low metal loading. The relatively large particle sizes observed were most likely due to the method of preparation used.

Silica was selected as the support for all further synthesised catalysts as it showed the highest selectivity to furfuryl alcohol.

Table 3 presents the activity of the commercial palladium catalysts at 25 °C and 100 °C and compares them to the activity of the synthesised 1.9%Pd/SiO_2. The reaction temperature seems to have no clear influence on the reaction. High conversions were achieved

Please cite this article in press as: Á. O'Driscoll, et al., The influence of metal selection on catalyst activity for the liquid phase hydrogenation of furfural to furfuryl alcohol, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.06.013

Table 3
A comparison of synthesised and commercial palladium catalysts. (Reaction conditions: 1 g catalyst, 25 ml FF, 175 ml solvent (ethanol), P_{H2} = 20 bar, t = 300 min).

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)
1.9%Pd/SiO_2 (Synthesised)	100	45	8
10%Pd/C (Sigma)	100	98	3
10%Pd/C (Sigma)	25	86	12
1%Pd/C (Sigma)	25	37	2

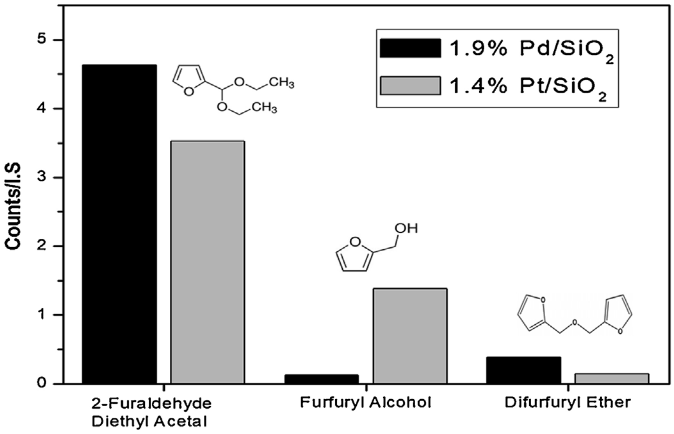

Fig. 4. Products detected at 35% furfural conversion for the indicated catalysts. (Reaction conditions: 1 g catalyst, 25 ml FF, 175 ml solvent (ethanol), P_{H_2} = 20 bar, T = 100 °C).

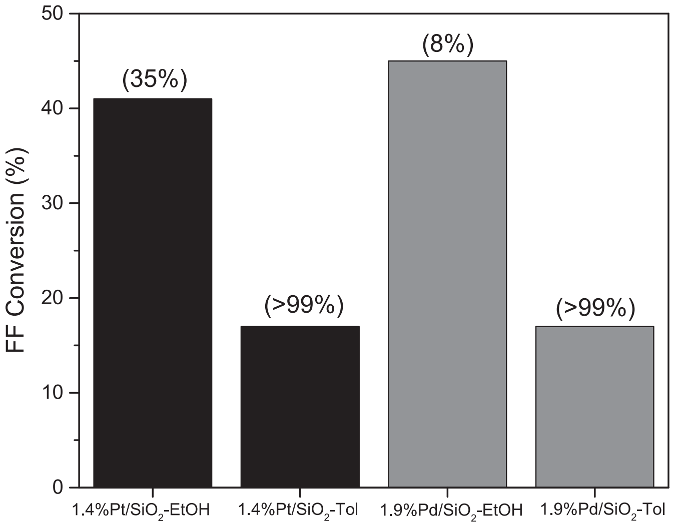

Fig. 5. The influence of metal selection and solvent selection on furfural conversion. The percentage selectivity to furfuryl alcohol is also included for each test. (Reaction conditions: 1 g catalyst, 25 ml FF, 175 ml Solvent, P_{H_2} = 20 bar, T = 100 °C, t = 300 min).

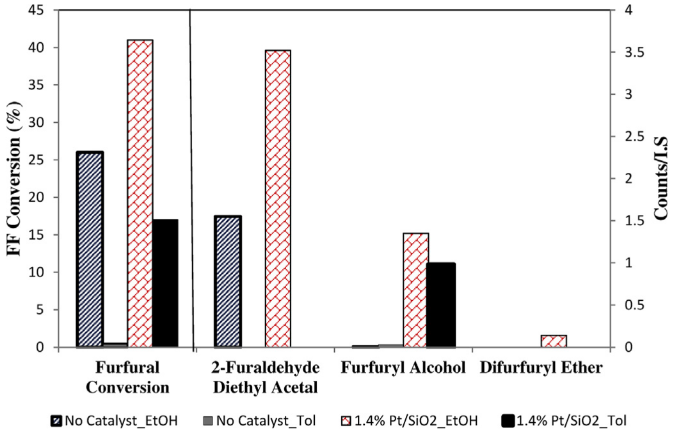

Fig. 6. The influence of solvent on furfural conversion and product formation. (Reaction conditions: no catalyst/1 g catalyst, 25 ml FF, 175 ml Solvent, P_{H_2} = 20 bar, T = 100 °C, t = 300 min).

when the palladium content of the catalyst was high (10 wt%). However, high conversions tended to lead to low product selectivity.

5.1. Identification of additional products

A more detailed study was carried out to investigate the reasons for the relatively low selectivity to furfuryl alcohol formation. The products formed following hydrogenation were analysed using GC–MS. Two additional products were identified and these were observed for all hydrogenations conducted in ethanol. These were difurfuryl ether and 2-Furaldehyde diethyl acetal. Indeed, the selectivity to the desired product furfuryl alcohol was low in the presence of ethanol. This was particularly true for the synthesised catalysts and can be seen in Fig. 4 which presents the reaction products of two synthesised catalysts 1.9%Pd/SiO_2 and 1.4%Pt/SiO_2 at 35% furfural conversion. These two catalysts were selected as, of all the catalysts prepared, they were the best in terms of furfural conversion and furfuryl alcohol selectivity respectively, as outlined in Table 1. The measurement in Fig. 4 is given in counts as difurfuryl ether is not commercially available preventing the preparation of a standard plot for calibration purposes. The product formed using the synthesised catalysts was primarily 2-furaldehyde diethyl acetal. This was followed by furfuryl alcohol and difurfuryl ether. The formation of the desired product furfuryl alcohol was low for both catalysts.

In order to investigate the influence of the solvent on furfural conversion, 1.9%Pd/SiO_2 and 1.4%Pt/SiO_2 were hydrogenated using ethanol (EtOH) and toluene (Tol) as solvents. The results of these tests are displayed in Fig. 5, which shows the conversion of furfural after 300 min hydrogenation and the selectivity to the desired product, furfuryl alcohol (values given in brackets). From this study, it was observed that furfural conversion is higher in the presence of ethanol with a slightly higher conversion observed using a palladium catalyst. Although conversion is lower when toluene is employed no difference in activity was observed between the two catalysts tested. Selectivity to furfuryl alcohol varied in ethanol with platinum giving a selectivity value (35%) over four times that of palladium (8%). Meanwhile, furfuryl alcohol was the principal product formed when toluene was used as solvent (99% selectivity for both catalysts). From this study it would seem that the platinum based catalyst is slightly better in terms of selectivity to the desired product, particularly in the presence of the ethanol solvent. Therefore this catalyst was studied in more detail. It is also clear from this study that the solvent has a major influence on the selectivity to the various products, particularly the desired product, furfuryl alcohol.

In order to further investigate the influence of the solvent, furfural hydrogenation tests were carried out in the absence and in the presence of the 1.4%Pt/SiO_2 catalyst using ethanol and toluene as solvent. The 1.4%Pt/SiO_2 catalyst was chosen as it was the most selective to furfuryl alcohol of the initial catalysts tested. The results from this study are displayed in Fig. 6 which shows the percentage conversion of furfural and the formation of both desirable and undesirable products (given in counts), in the absence and presence of the catalyst. Two solvents were investigated, ethanol and toluene. It was observed that in the absence of a catalyst conversion was very low using toluene as the solvent coupled with low product formation. Furfural conversion was significantly higher,

Please cite this article in press as: Á. O'Driscoll, et al., The influence of metal selection on catalyst activity for the liquid phase hydrogenation of furfural to furfuryl alcohol, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.06.013

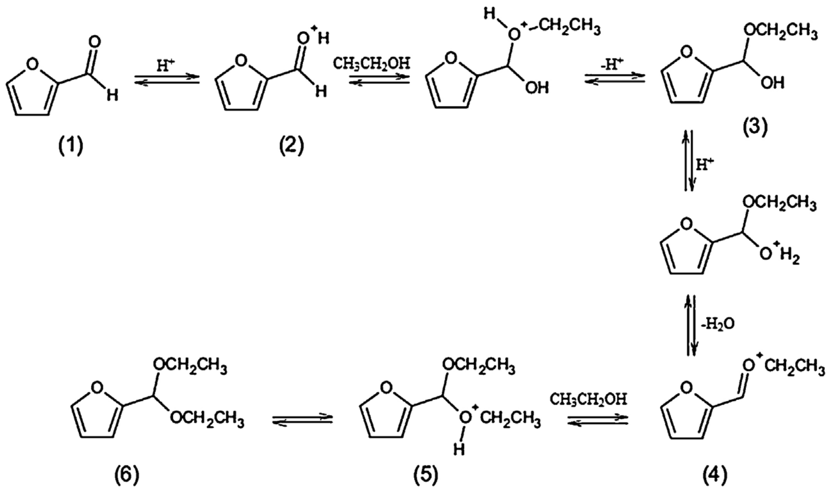

Fig. 7. The reaction pathway for the acetalization of furfural to 2-furaldehyde diethyl acetal.
Source: adapted from Rubio-Caballero et al. [45].

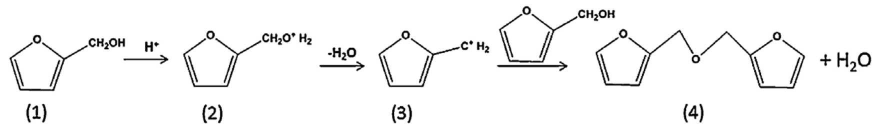

Fig. 8. The reaction pathway for the etherification of furfuryl alcohol to difurfuryl ether.
Source: adapted from Zhang et al. [47].

in the absence of a catalyst, using ethanol as the solvent with 2-furaldehyde diethyl acetal observed as the primary product. This indicated that a reaction occurred between ethanol and furfural in the homogeneous phase under the conditions studied. When a catalyst was used, the conversion was higher for both solvents. It was observed that using ethanol, furfuryl alcohol and 2-furfuraldehyde diethyl acetal were formed while the use of toluene had a lower furfural conversion but furfuryl alcohol was the main product formed with minimal quantities of other by-products observed.

The results shown in Fig. 6 clearly indicate that 2-Furaldehyde diethyl acetal is only formed in large quantities when ethanol is present. In the presence of toluene, 2-furaldehyde diethyl acetal was absent. The production of furfuryl alcohol was higher when a catalyst was used with results indicating that a catalyst is essential for the desired reaction to occur. The production of furfuryl alcohol is higher when ethanol is employed, most likely resulting from the higher furfural conversion observed with the use of ethanol. The production of difurfuryl ether was only observed in the presence of a catalyst using ethanol as solvent. Generally, the use of toluene as a solvent resulted in the production of furfuryl alcohol only but conversion was higher when ethanol was used.

In Table 1, the catalysts 0.9%Ni/SiO_2, 1.1%Cu/SiO_2, 1.9%Ni/SiO_2 and 2% Cu/SiO_2 all presented relatively similar furfural conversion (~30%) in the presence of ethanol solvent. From Fig. 6 it can be seen that in the absence of a catalyst, 26% conversion is achieved. This would indicate that the nickel and copper based catalysts are not active for furfural conversion under the conditions studied and the conversions observed in Table 1 are primarily the result of the liquid phase non-catalytic acetalization reaction.

The proposed reaction pathway for the formation of 2-furaldehyde diethyl acetal is presented in Fig. 7 while that for difurfuryl ether is presented in Fig. 8. The carbonyl group of furfural (1) is protonated from a H^+ ion sourced from ethanol or a catalyst to form an intermediate (2). Ethanol reacts with this intermediate forming the hemiacetal. A proton is removed from the hemiacetal which subsequently re-protonates and dehydrates to form another intermediate (4). This intermediate then reacts with another ethanol molecule giving an intermediate (5) which is deprotonated to form 2-furaldehyde diethyl acetal (6) [45,46]. The etherification of furfuryl alcohol pathway shown in Fig. 8 begins with the protonation of furfuryl alcohol (1), where it is proposed that the H^+ ion is available from the ethanol or a catalyst. This step results in a protonated intermediate (2) which is dehydrated to form an additional intermediate (3) that in turn reacts with another furfuryl alcohol molecule to form difurfuryl ether (4) [47–49]. In this work, these products were observed in the absence of a catalyst therefore the H^+ ion is most likely sourced from the solvent ethanol rather than the catalyst.

Table 4
Prepared platinum supported on silica catalysts.

Catalyst	Expected Pt Weight Loading (%)	Measured Pt Weight Loading (%)
Pt/SiO_2	0.5	0.3
Pt/SiO_2	1	0.9
Pt/SiO_2	2	1.9

6. Development of platinum catalysts

From the initial catalysts tested, platinum was observed as the superior metal for furfuryl alcohol production. The development of palladium catalysts resulted in relatively low furfuryl alcohol selectivities despite the increase in furfural conversion therefore it was decided to investigate the platinum based catalysts in more detail. The influence of platinum metal loading on furfural conversion was investigated by synthesising a series of platinum catalysts by wet impregnation using silica as the support, these catalysts are listed in Table 4.

Fig. 9 shows the percentage furfural conversion for the prepared platinum supported silica catalysts with reaction time. The results show that furfural conversion for 0.9%Pt/SiO_2 and 1.9%Pt/SiO_2 are relatively similar with no difference after 300 min reaction time

Please cite this article in press as: Á. O'Driscoll, et al., The influence of metal selection on catalyst activity for the liquid phase hydrogenation of furfural to furfuryl alcohol, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.06.013

Table 5
Catalysts produced by surface organometallic catalysis.

Metal	Electronegativity (Pauling)	Actual Metal Loading	Actual Platinum Loading
Platinum (Pt)- Base	2.28	–	0.9
Tin (Sn)	1.96	0.4	0.6
Molybdenum (Mo)	2.16	0.2	0.6
Manganese (Mn)	1.55	0.3	0.6
Barium(Ba)	0.89	0.2	0.6
Iron (Fe)	1.83	0.2	0.6
Nickel (Ni)	1.91	0.5	0.6

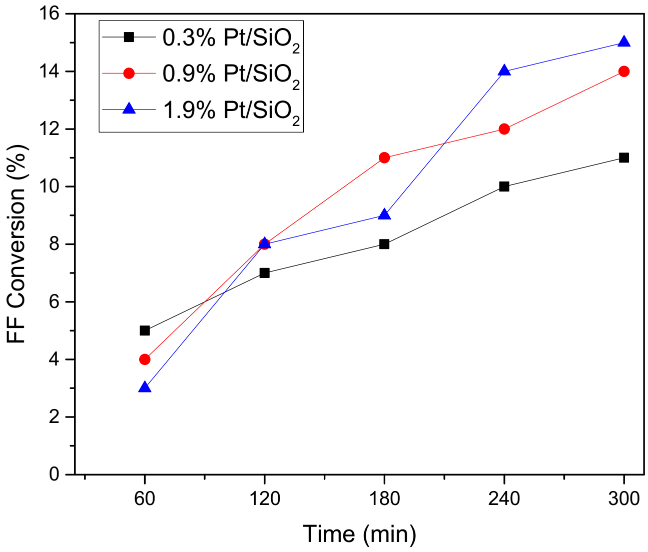

Fig. 9. The influence of metal loading on furfural conversion. (Reaction conditions: 1 g catalyst, 25 ml FF, 175 ml solvent (toluene), P_{H_2} = 20 bar, T = 100 °C).

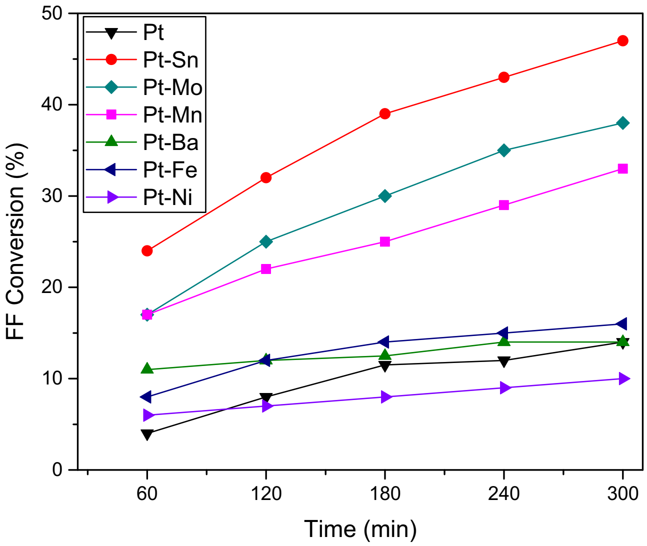

Fig. 10. The influence of a variety of promoters on the monometallic platinum base catalyst. (Reaction conditions: 1 g catalyst, 25 ml FF, 175 ml solvent (toluene), P_{H_2} = 20 bar, T=100 °C).

and considerably better than 0.3%Pt/SiO$_2$. This result is most likely due to the dispersion of platinum on the support. As the platinum loading increased it is possible that metal agglomeration occurred resulting in low platinum dispersion. It is well known that low metal dispersions can lead to poor catalytic activities [50]. Selectivity to furfuryl alcohol was close to 100% for all catalysts. Thus, after considering all factors, a Pt/SiO$_2$ catalyst with a desired 1 wt% loading was selected for future work involving the investigation of using bimetallic catalysts.

The research into bimetallic catalysts focused on the synthesis of catalysts by controlled surface reactions as the method was observed in literature to produce catalysts with low metal loadings together with good activity and was therefore suited to industrial requirements. A variety of metals were selected to act as promoters of the selected base catalyst, 1%Pt/SiO$_2$. This assortment included tin, molybdenum, manganese, barium, iron and nickel. These metals were selected according to published trends as Tathod and Dhepe [51] state that the addition of promoter metals which have an electron deficient state in the bimetallic catalyst are superior hydrogenation catalysts as they polarise the furfural carbonyl group. Meanwhile, Merlo et al. [28] suggested that the difference in electronegativity of the metals in the bimetallic system also influences the activity of the catalyst. A promoter metal which is more electropositive than the base metal is deemed the best as it increases interaction with the furfural carbonyl group. Research undertaken by the group was directed at increasing the selectivity of the reaction to furfuryl alcohol. However, the principle was applied to this work with a view to increasing furfural conversion. The electronegativities of the selected metals are shown in Table 5 which illustrates that a varied range of metals which are more electropositive than platinum were selected. A more electronegative metal than platinum was not selected for comparison as platinum is one of the most electronegative metals.

A complete list of the catalysts examined is shown in Table 5. The expected metal loadings for the promoter metal and the platinum were 0.4% and 1% respectively.

All catalysts were tested for the hydrogenation of furfural to furfuryl alcohol using the same reaction conditions. Fig. 10 shows the conversion of furfural with reaction time for all the prepared bimetallic catalysts and these are compared to the monometallic platinum catalyst. The platinum loading of these bimetallic catalysts was similar as all were synthesised by wet-impregnation from a single batch. However, some variation was observed for the loading of the promoter metals which were deposited by surface reactions. These variations are most likely due to issues arising from the stirred metal solution used in the catalyst synthesis. This includes low solubility of the metal salt and insufficient degassing causing reduced metal deposition.

The monometallic platinum catalyst achieved 14% furfural conversion after 5 h. Overall, the addition of a second metal was seen to have a positive influence on the desired reaction with the exception of nickel. Several of the promoter metals studied resulted in a significant increase in furfural conversion including manganese and molybdenum, obtaining 33% and 38% conversion respectively. However, the bimetallic catalysts containing Pt-Ni, Pt-Fe and Pt-Ba yielded furfural conversion similar to the monometallic platinum catalyst. Tin was found to have the most significant influence by increasing the furfural conversion to 47%.For the conditions studied, selectivity to furfuryl alcohol did not vary across the metal selection, remaining close to 100% for all prepared catalysts.

The influence of each promoter metal studied was clearly observed however no correlation was found between the elec-

Please cite this article in press as: Á. O'Driscoll, et al., The influence of metal selection on catalyst activity for the liquid phase hydrogenation of furfural to furfuryl alcohol, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.06.013

tronegativities of the metals investigated and their influence on the furfural conversion. The difference in electronegativity of promoter metals was previously studied [29] to investigate furfuryl alcohol selectivity and side-product formation. A comparable influence on the furfural conversion as studied in this research was not observed. The best catalyst in terms of activity was found to be the Pt-Sn bimetallic catalyst although the reason for this improvement is not clear and warrants further investigation. However, from the literature the Pt-Sn catalyst has been shown to be a successful catalyst for a wide variety of reactions. The improvement in activity has been linked to both geometrical structural changes [52] and electronic modifications [53]. The reason for the improved activity in this work is not clear and will need to be studied in more detail.

7. Conclusions

1.9%Pd/SiO_2 and 1.4%Pt/SiO_2 were identified as promising catalysts for the liquid phase hydrogenation of furfural. Of a series of supports investigated (SiO_2, Al-SBA-15, ß-zeolite and TiO_2), SiO_2 was the superior support as it gave the best furfuryl alcohol selectivity. Subsequent comparisons to commercial palladium catalysts found that palladium presents good furfural conversion but was not selective to furfuryl alcohol.

Two undesired products were formed, 2-furaldehyde diethyl acetal and difurfuryl ether when ethanol was used as the solvent. The production of these undesirable products was significantly reduced or eliminated when toluene was employed as solvent.

Platinum based catalysts presented high selectivity to furfuryl alcohol. A variety of weight loadings in the range of 0.5–2 wt% were tested and 1%Pt/SiO_2 was selected for further research of bimetallic catalysts. From the bimetallic catalysts studied, Pt-Sn was the most active for the hydrogenation of furfural to furfuryl alcohol.

Acknowledgements

The Earth and Natural Sciences Doctoral Studies Programme is funded under the Programme for Research in Third-Level Institutions and co-funded under the European Regional Development Fund.

The authors would like to acknowledge the research group of Prof Ursel Bangert for their contribution to the TEM analysis in this publication.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2016.06.013.

References

[1] Council Directive (EC) 2009/28/EC of 23 (2009) on promotion of the use of energy from renewable sources, (2009).
[2] D.J. Hayes, M.H.B. Hayes, Biofuels. Bioprod. Biorefin. 3 (2009) 500.
[3] G. Centi, P. Lanzafame, S. Perathoner, Catal. Today 167 (2011) 14.
[4] A.S. Dias, S. Lima, M. Pillinger, A.A. Valente, Catal. Lett. 114 (2007) 151.
[5] A.S. Dias, S. Lima, D. Carriazo, V. Rives, M. Pillinger, A.A. Valente, J. Catal. 244 (2006) 230.
[6] K. Dussan, B. Girisuta, D. Haverty, J.J. Leahy, M.H.B. Hayes, Bioresour. Technol. 149 (2013) 216.
[7] X.J. Shi, Y.L. Wu, H.F. Yi, G. Rui, P.P. Li, M.D. Yang, G.H. Wang, Energies 4 (2011) 669.
[8] W. Riansa-ngawong, P. Prasertsan, Carbohydr. Res. 346 (2011) 103.
[9] K. Dussan, B. Girisuta, M. Lopes, J.J. Leahy, M.H.B. Hayes, ChemSusChem 8 (2015) 1411.
[10] K.J. Zeitsch, The Chemistry and Technology of Furfural and Its Many By-products: Sugar Series 13, Elsevier Science, NL, 2000.
[11] W. Huang, H. Li, B. Zhu, Y.F. feng, S. Wang, S. Zhang, Ultrason. Sonochem. 14 (2007) 67.
[12] B.M. Nagaraja, A.H. Padmasri, B.D. Raju, K.S.R. Rao, Int. J. Hydrogen Energy 36 (2011) 3417.
[13] C. Xu, L. Zheng, D. Deng, J. Liu, S. Liu, Catal. Commun. 12 (2011) 996.
[14] A.S. Dias, S. Lima, M. Pillinger, A.A. Valente, Carbohydr. Res. 341 (2006) 2946.
[15] W.B.a.T. Services, Furfural chemicals and biofuels from agriculture, A report for the rural industries research and development corporation Sydney, (2006).
[16] S. Sitthisa, D.E. Resasco, Catal. Lett. 141 (2011) 784.
[17] Z. Xinghua, W. Tiejun, M. Longlong, W. Chuangzhi, Fuel 89 (2010) 2697.
[18] X.F. Chen, H.X. Li, H.S. Luo, M.H. Qiao, Appl. Catal. A 233 (2002) 13.
[19] M.M. Villaverde, T.F. Garetto, A.J. Marchi, Catal. Commun. 58 (2015) 6.
[20] R.V. Sharma, U. Das, R. Sammynaiken, A.K. Dalai, Appl. Catal. A 454 (2013) 127.
[21] K. Yan, A. Chen, Fuel 115 (2014) 101.
[22] S. Srivastava, N. Solanki, P. Mohanty, K.A. Shah, J.K. Parikh, A.K. Dalai, Catal. Lett. 145 (2015) 816.
[23] S. Wei, H. Cui, J. Wang, S. Zhuo, W. Yi, L. Wang, Z. Li, Particuology 9 (2011) 69.
[24] S.P. Lee, Y.W. Chen, Ind. Eng. Chem. Res. 38 (1999) 2548.
[25] B.J. Liaw, S.J. Chiang, C.H. Tsai, Y.Z. Chen, Appl. Catal. A 284 (2005) 239.
[26] R. Rodiansono, T. Hara, N. Ichikuni, S. Shimazu, Bull. Chem. React. Eng. Catal. 9 (2014) 53.
[27] V. Vetere, A.B. Merlo, J.F. Ruggera, M.L. Casella, J. Braz. Chem. Soc. 21 (2010) 914.
[28] A.B. Merlo, V. Vetere, J.M. Ramallo-Lopez, F.G. Requejo, M.L. Casella, React. Kinet. Mech. Catal. 104 (2011) 467.
[29] A.B. Merlo, V. Vetere, J.F. Ruggera, M.L. Casella, Catal. Commun. 10 (2009) 1665.
[30] W. Yu, Y. Tang, L. Mo, P. Chen, H. Lou, X. Zheng, Bioresour. Technol. 102 (2011) 8241.
[31] W. Yu, Y. Tang, L. Mo, P. Chen, H. Lou, X. Zheng, Catal. Commun. 13 (2011) 35.
[32] K. Fulajtárova, T. Soták, M. Hronec, I. Vávra, E. Dobročka, M. Omastová, Appl. Catal. A 502 (2015) 78.
[33] L. Baijun, L. Lianhai, W. Bingchun, C. Tianxi, I. Katsuyoshi, Appl. Catal. A 171 (1998) 117.
[34] P. Reyes, D. Salinas, C. Campos, M. Oportus, J. Murcia, H. Rojas, G. Borda, J.L. Garcia Fierro, Quim. Nova 33 (2010) 777.
[35] D. Liu, D. Zemlyanov, T. Wu, R.J. Lobo-Lapidus, J.A. Dumesic, J.T. Miller, C.L. Marshall, J. Catal. 299 (2013) 336.
[36] L.R. Baker, G. Kennedy, M. Van Spronsen, A. Hervier, X. Cai, S. Chen, L.-W. Wang, G.A. Somorjai, J. Am. Chem. Soc. 134 (2012) 14208.
[37] M.J. Taylor, L.J. Durndell, M.A. Isaacs, C.M.A. Parlett, K. Wilson, A.F. Lee, G. Kyriakou, Appl. Catal. B 180 (2016) 580.
[38] R.V. Maligal-Ganesh, C. Xiao, T.W. Goh, L.-L. Wang, J. Gustafson, Y. Pei, Z. Qi, D.D. Johnson, S. Zhang, F. Tao, W. Huang, ACS Catal. 6 (2016) 1754.
[39] R. Srivastava, D. Srinivas, P. Ratnasamy, Microporous Mesoporous Mater. 90 (2006) 314.
[40] D.A. Bulushev, S. Beloshapkin, J.R.H. Ross, Catal. Today 154 (2010) 7.
[41] A. Corma, M.E. Domine, S. Valencia, J. Catal. 215 (2003) 294.
[42] J. Luo, J. Yu, R.J. Gorte, E. Mahmoud, D.G. Vlachos, M.A. Smith, Catal. Sci. Technol. 4 (2014) 3074.
[43] P. Lanzafame, D.M. Temi, S. Perathoner, G. Centi, A. Macario, A. Aloise, G. Giordano, Catal. Today 175 (2011) 435.
[44] J. Iglesias, J.A. Melero, G. Morales, J. Moreno, Y. Segura, M. Paniagua, A. Cambra, B. Hernandez, Catalysts 5 (2015) 1911.
[45] J.M. Rubio-Caballero, S. Saravanamurugan, P. Maireles-Torres, A. Riisager, Catal. Today 234 (2014) 233.
[46] H. Rojas, G. Borda, D. Rosas, J.J. Martinez, P. Reyes, Dyna-Colombia 75 (2008) 115.
[47] Z. Zhang, C.U. Pittman Jr., S. Sui, J. Sun, Q. Wang, Energies 6 (2013) 1568.
[48] E.M. Wewerka, E.D. Loughran, K.L. Walters, J. Appl. Polym. Sci. 15 (1971) 1437.
[49] E. Fillion, The development of new oxabicyclic-based strategies for the stereo- and enantioselective synthesis of azepines, in: Thiepines and Thiocines, Polysubstituted Decalins and Related Fused Polycycles, Chemistry, Vol. PhD, University of Toronto, Toronto, 1998, p. 364.
[50] R. Portela, V.E. Garcia-Sanchez, M. Villarroel, S.B. Rasmussen, P. Avila, Appl. Catal. A: Gen. 510 (2016) 49.
[51] A.P. Tathod, P.L. Dhepe, Bioresour. Technol. 178 (2015) 36.
[52] F.E. López-Suárez, C.T. Carvalho-Filho, A. Bueno-López, J. Arboleda, A. Echavarría, K.I.B. Eguiluz, G.R. Salazar-Banda, J. Int. Hydrogen Energy 40 (2015) 12674.
[53] J.H. Kim, S.M. Choi, S.H. Nam, M.H. Seo, S.H. Choi, W.B. Kim, Appl. Catal. B: Environ. 82 (2008) 89.

Please cite this article in press as: Á. O'Driscoll, et al., The influence of metal selection on catalyst activity for the liquid phase hydrogenation of furfural to furfuryl alcohol, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.06.013