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Batch *vs.* continuous flow performance of supported mono- and bimetallic nickel catalysts for catalytic transfer hydrogenation of furfural in isopropanol

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Abstract: Furfural takes an important position in hemicelluloses biorefinery platforms. It can be converted into a wide range of chemicals. One important valorization route is the catalytic hydrogenation. Whereas molecular hydrogen is mostly used in industrial hydrogenation processes, recent studies also showed that alcohols can be used as reductants from which hydrides can be transferred catalytically to furfural. This process is often assisted by the formation of significant amounts of side products, in despite of high yields to the hydrogenolysis product 2-methylfuran. The present work explores the catalytic behavior in batch and continuous flow of mono- and bimetallic nickel catalysts supported on activated carbon for the catalytic transfer hydrogenation of furfural in isopropanol.

Introduction

Hemicelluloses are a heterogeneous carbohydrate fraction and can potentially provide a wide range of compounds to replace current chemicals derived from crude oil.^[1] The main disadvantage of their heterogeneity is the fact that C-5 sugars are not converted biochemically as efficient as C-6 sugars (using whole cells or enzymes). Therefore, the chemocatalytic valorization of hemicelluloses and their co-generated waste streams is an imminent research area. Recent advances in the catalytic valorization of hemicelluloses envision the conversion to levulinates, lactones and furans,^[2,3] either in one-pot conversion step^[4] or in multiple steps via the hydrolysis to oligomers and xylose (as the most abundant monomer).^[5] The catalytic route to furfural through dehydration and isomerization today is still challenging route. Once furfural is produced, it can

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be converted into a wide range of chemicals, either by catalytic oxidation,^[6] amination^[7] or hydrogenation (Scheme 1a).^[3] The hydrogenation route is a highly reported research area, as it can provide a wide range of bulk chemicals. Although promising results have been reported on catalytic furfural hydrogenation in vapor phase, most of the studies aim liquid phase hydrogenation, mainly because catalyst deactivation through coke formation occurs faster in the former.^[3] High selectivity to furfuryl alcohol (FA) has been demonstrated for numerous catalysts,^[8-17] as the product of the first step in the hydrogenation pathway (Scheme 1b). Only few studies reported high selectivity to 2-methylfuran (MF).^[12,18] The production of MF is attractive, as it has a very low boiling point which enables efficient separation. MF has shown superior performance as an additive in gasoline fuels compared to other furfural hydrogenation products.^[19] The conversion to MF occurs via hydrogenolysis of the C-O linkage in FA, which in general requires higher temperature and longer reaction time. Beneficial effects on the selectivity to MF have been reported for bimetallic catalysts.^[12,18,20] The type of catalyst support also plays an important role in the hydrogenation of furfural. Supports often include Lewis acids, such as γ -Al₂O₃,^[14,21,22] TiO₂,^[12,16,23] ZrO_2 ,^[8] CeO_2 ,^[14] SiO_2 ,^[9,10] and AI-SBA-15,^[24] basic metal oxides (MgO and ZnO)^[11,14] and base metal carbonates (CaCO₃),^[10] which assist in polarizing the furfural carbonyl bond and which can actively take part in one of the reaction pathways. More neutral supports such as carbons were also used in some studies.[10,13,18,24,25]

Molecular hydrogen (H₂) is mostly used as the reductant for catalytic furfural hydrogenation.[8-15,21-25] The reduction by catalytic hydrogen transfer in various alcohols (ROH), however, is reported only in few cases.^[17,18,20] The latter is attractive, not only from the techno-economic point of view, but also because the interphase transfer is improved (solid/liquid for ROH vs. solid/liquid/gas for H₂). Important mechanistic insights were reported by Gilkey et al. (2015), who demonstrated that when starting from FA the hydrogenolysis via ring activation (Scheme 2a) was predominant over direct metal-mediated hydrogenolysis (Scheme 2b), eventually leading to the formation of water. Based on isotopic kinetic effects, it was also found that in the first step of the hydrogenation (formation of FA), the transfer of hydrides from isopropanol to furfural mainly occurs through formation of a complex between furfural, ROH and Lewis acid sites (Scheme 2c), rather than production of H₂ from ROH on the metal surface (Scheme 2d). Gilkey et al. (2015) also concluded that strong adsorption of furfural retards the metal catalyzed pathway (competitive adsorption of furfural and ROH on the metal site), but does not affect the Lewis acid-mediated hydrogen transfer pathway because of its concerted bulky

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nature in which ROH coordinates a hydrogen directly to the carbonyl group in furfural (no competition on the metal site). High selectivity to MF in catalytic hydrogen transfer can be promoted by inducing a metal oxide phase (acting as Lewis acid) co-existing along with the metal phase,^[18,20] to catalyze the hydride transfer and to bind OH groups released upon hydrogenolysis of FA.

Based on these findings, the present study aims to explore the extent of catalytic hydrogen transfer to furfural in isopropanol (*i*-PrOH), using monometallic (Ni) and bimetallic (Ni-W) nickel catalysts supported on neutral micro/mesoporous activated carbon. The experiments were conducted both in batch and in continuous flow to study the effect on the catalyst performance. Fresh and used catalysts were analyzed with XRD, XPS and ICP-MS to study the catalyst deactivation.



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Scheme 2. (a) Furfuryl alcohol (FA) hydrogenolysis via ring activation, (b) direct FA hydrogenolysis, (c) Meerwein-Ponndorf-Verley reduction of furfural and (d) metal-mediated intermolecular hydride transfer to furfural.

Results and Discussion

Catalyst characterization. A series of monometallic (5%Ni/AC and 10%Ni/AC) and bimetallic (5%Ni-15%W/AC and 10%Ni-15%W/AC) nickel-based catalysts were synthesized via classic wet impregnation on commercial activated carbon (AC), followed by thermal treatment in inert and H₂ atmosphere. The AC (catalyst support) was a neutral carbon (pH 6-8) and contained only small amounts of Lewis acid sites.^[26] The catalyst samples were stored under ambient atmosphere and were used as such for catalytic experiments and characterization. They were characterized by nitrogen (N₂) porosimetry; the corresponding N₂ adsorption-desorption isotherms are shown in Figure 1a. The parent AC is a microporous carbon with a high contribution of meso/macroporosity (Table 1, entry 1). About 65 % of its total surface area and 36 % of its total pore volume is attributed to micropores and the remaining to meso/macropores and external surface, as revealed from the isotherm shapes, where a progressive increase of adsorbed N2 can be observed over the whole P/Po range, indicating the presence of a relatively disordered network of meso- and macropores. As a result of this size inhomogeneity, no distinct peaks in the BJH pore size distribution curves were observed, while only a weak peak was identified in the DFT pore size distribution curve with an average diameter of 3.4 nm. The total and micropore surface area, as well as the pore volumes of the monometallic loaded AC catalysts were essentially unchanged compared to those of the parent AC (max. 10 % decrease). The porosity characteristics of the bimetallic catalysts decreased by ca. 30 %, as determined for the 10%Ni-15%W/AC catalyst. The catalysts were also characterized by powder XRD analysis. The corresponding diffraction patterns are shown in Figure 1b. The 5%Ni/AC catalyst consisted essentially of metallic Ni(0) nanoparticles with

average crystal size 6.8 nm. As the Ni content increased to 10%, the Ni(0) crystal size increased to 23.2 nm and a NiO phase appears with crystal size 6.1 nm. In the case of bimetallic catalysts, and more specifically in 5%Ni-15%W/AC, the crystalline phases of tungsten oxide (WO₂) and nickel tungsten oxide (NiWO₄) prevail with average crystal sizes 9.9 and 15.5 nm, respectively. However, for the 10%Ni-15%W/AC catalyst, the dominant peak in the XRD pattern pertains to Ni(0) with crystal size 10.7 nm, being markedly lower than the Ni(0) crystal size in the monometallic 10%Ni/AC catalyst.

Table 1.	Porosity	of	mono-	and	bimetallic	Ni	catalysts	supported	on
activated carbon (AC).									

Catalyst	Total SSA (m²/g) ^[a]	Total pore volume (cc/g) ^[b]	Micropore area (m²/g) & volume (cc/g) ^[c]	Meso/macro- pore & external area (m ² /g) & volume (cc/g) ^[d]
AC	1280	0.95	840 / 0.34	440 / 0.60
5%Ni/AC	1250	0.88	830 / 0.34	420 / 0.54
10%Ni/AC	1250	0.90	810 / 0.33	440 / 0.57
5%Ni- 15%W/AC	1020	0.72	680 / 0.28	350 / 0.44
10%Ni- 15%W/AC	920	0.64	610 / 0.25	310 / 0.39

[a] SSA: specific surface area from N₂ sorption at -196 °C (multi-point BET method). [b] Total pore volume at P/P₀ = 0.99. [c] t-plot method. [d] Meso/macropore & external area = Total SSA - Micropore area; Meso/macropore volume = Total pore volume - Micropore volume (t-plot)

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Figure 1. (a) N₂ adsorption-desorption isotherms of the parent calcined activated carbon (AC) and the supported mono- and bimetallic Ni catalysts and (b) corresponding XRD patterns (symbols indicate the respective crystalline phase: (*) for Ni(0) and (•) for NiO, (\blacktriangle) for WO₂, and (\triangle) for NiWO₄).

Batch furfural hydrogenation experiments. The experiments in batch were carried out for 5 h using a 0.35 M furfural feedstock in isopropanol (*i*-PrOH). **Table 2** shows the results obtained with the monometallic catalysts (entries 3-4), as well with the bimetallic Ni-W catalysts (entries 5-8). Furfuryl alcohol (FA) and 2-methylfuran (MF) were the only products produced in significant amounts, whereas the corresponding rina hydrogenated products tetrahydrofurfuryl alcohol (THFA) and 2methyltetrahydrofuran (MTHF) were produced only in small amounts (0-3 %). The blank experiment (entry 1) gave only 2 % conversion of furfural. With the monometallic 5%Ni/AC catalyst, but in the absence of molecular hydrogen (H₂), 10 % conversion was observed (entry 2). Much higher conversion (85 %) was observed with the same catalyst when 30 bars of H₂ was used (entry 3), with high selectivity (78 %) to MF. To the best of our knowledge, the corresponding MF yield is among the highest reported in literature at temperatures ≤ 200 °C.^[12,18,20] The bimetallic Ni-W catalysts (entries 5 and 7) gave moderate conversions (ca. 50 %), with 30-40 % selectivity to MF. At 260 °C without the addition of H₂ (entries 6 and 8), the conversions reached 95 and 83 % for the mono- and bimetallic catalyst, respectively. The selectivity to MF, however, was much higher for the monometallic (53 %) than for the bimetallic catalyst (7 and 39 % for 5%-15%W/AC and 10%Ni-15%W/AC, respectively). These results show that higher furfural conversion can be obtained through catalyzed hydrogen transfer from i-PrOH to furfural, by operating at 260 °C instead of 200 °C, however with lower selectivity to MF. What did seem to occur is that at 260 °C and without H₂, a substantial higher amounts of side products were produced, as seen from the significant lacks in the mass balance (entries 4, 6 and 8). Side products were only detected using the GC-FID conditions used for product analysis after batch experiments. In one experiment (entry 3), after removing the solvent (i-PrOH) and MF by rotavaporisation, 2-(isopropoxy)methylfuran (iPrOMF) was identified using ¹H-NMR and ¹³C-NMR (results not shown), in agreement with the literature.^[15-17,20,27] This is the alkyl ether side product from FA and i-PrOH (Meerwein-Ponndorf-Verley reduction).

 Table 2. Conversion and product yields after 5 h batch hydrogenation of 0.35 M furfural in 60 mL *i*-PrOH (FA: furfure alcohol, MF: 2-methylfuran, THFA: tetrahydrofurfuryl alcohol and MTHF: 2-methyltetrahydrofuran).

Entry	Catalyst	т	H₂ (bars)	Conversion (%)	1		Yield	Mass balance (0()		
Linuy		(°C)			FA	MF	THFA	MTHF	iPrOMF	
1	-	200	30	2	6	1	0	0	0	105
2	5%Ni/AC	200	0	10	10	1	0	0	0	101
3	5%Ni/AC	200	30	85	6	66	1	2	3	93
4	5%Ni/AC	260	0	95	20	50	1	1	1	78
5	5%Ni-15%W/AC	200	30	50	32	15	1	2	4	104
6	5%Ni-15%W/AC	260	0	83	16	6	1	2	6	48 ^c
7	10%Ni-15%W/AC	200	30	51	8	20	1	3	9	90
8	10%Ni-15%W/AC	260	0	83	25	6	1	2	8	59 ^d

^c Unknown compounds U1 and U2 eluting at 10.4 and 12.0 min in GC-FID analysis not included (39 % of total peak area)^{; d} Unknown compounds U1 and U2 accounted for 21 % of total peak area

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This side product probably corresponded with the unidentified peak at 7.0 min in the corresponding chromatograms (see **Figure S1** in the Supporting Information). Only in the experiments with bimetallic catalysts (entries 6 and 8), two other peaks were detected at higher retention times (10.4 and 12.0 min). Other side products may include (hemi)-acetals (via dehydration) and FA polymerization products, but these were not identified in the present study. Based on the GC retention times of the pure standards 1,4-pentanediol, 1,2- pentanediol, 1,5- pentanediol, furan and tetrahydrofuran, it was confirmed that no ring-opening neither decarbonylation occurred.

Continuous flow hydrogen transfer experiments. All continuous flow experiments were performed without the supply of H₂. First, the 5%Ni/AC catalyst (110 mg) was tested continuously using a 0.2 M furfural feedstock in *i*-PrOH, gradually moving from low (200 °C) to high (260 °C) temperature and for each temperature from high (0.4 mL min⁻¹) to low (0.1 mL min⁻¹) flow rate (**Figure 2a**). The total time on stream was *ca*. 9 h. Conversions increased with lower flow rates and with higher temperatures. During the first hour on stream the selectivity to MF was fare (20-30 %), but then gradually dropped over time, even at higher temperatures. The results suggested that substantial catalyst deactivation occurred.



Figure 2. Conversion (gray scale) and selectivity to FA (blue) and MF (red) in continuous flow transfer hydrogenation in *i*-PrOH, using (a) 5%Ni/AC, 0.2 M furfural and 0 bar, (b) 0.2 M furfural, 260 °C, 0 bar and (c) 0.1 M furfural, 230 °C and 30 bars.

Among different fresh catalysts, each tested during 3 h on stream at 260 °C (Figure 2b), 5%Ni/AC provided the highest conversion at low flow rate (0.1 mL min⁻¹) while 10%Ni/AC gave higher conversion at higher flow rate (0.2-0.4 mL min⁻¹). These monometallic catalysts were more active compared to bimetallic 5%Ni-15%W/AC and to 5%Raney-Ni/AC, a catalyst with high hydrogen transfer activity in combination with i-PrOH, as demonstrated by Wang and Rinaldi for various bio-oil derived compounds at temperatures already starting from 120 °C.28 The selectivity to MF was however much lower, in strong contrast with the batch results. Interestingly, the selectivity to MF with bimetallic Ni-W in the continuous flow experiment at 0.1 mL min-¹ reached 98 %. Improved conversions were obtained by increasing the hydrodynamic pressure from 0 to 30 bars and using a smaller furfural feed load (0.1 M) as demonstrated in Figure 2c, where 5%Ni/AC gave the highest conversion (similar to 5%Pd/C), while 5%Ni-15%W/AC gave the highest selectivity to MF.

Further experiments were conducted under optimized conditions to compare the operational stability of monometallic Ni and bimetallic Ni-W catalysts. With the monometallic catalysts (**Figures 3a** and **3b**) a peak in the FA production was observed during the first hour on stream, which then dropped followed by a slow increase over time. With the bimetallic catalysts in turn

(Figure 3c and 3d), no significant amounts of FA were produced at any point in contrast with the batch results (Table 2, entries 6 and 8). As well in contrast to batch experiments, the bimetallic catalysts showed very high selectivity to MF, ca. 85 and 84 % for the 5%Ni-15%W/AC and 10%Ni-5%W/AC catalysts, respectively, as the mean selectivity calculated over the 0.7-7.0 h period on stream. The conversion in turn decreased from 85 to 27 % and from 99 to 11 %, respectively, showing their lower operational stability compared to the monometallic catalysts (conversions dropped faster over time). Still, after 6 h the MF yields produced with the bimetallic catalysts (13-32 %) were higher than the ones produced with monometallic catalysts (6-20 %), because the bimetallic ones retained their high selectivity to MF. Selectivities slightly higher than 100 % were observed at some points with both bimetallic Ni-W catalysts, which was probably the result of kinetic sorption effects. A significant amount of products remained unknown when using monometallic catalysts (mass balance 35-75 % for the monometallic vs. 74-105 % for the bimetallic catalysts). These results indicate that side product formation is suppressed with the bimetallic catalysts, in favor of MF formation. Acetone formation and gas bubbles production was observed in most of the experiments, although with decreasing trend over time (deactivation of metal-mediated hydrogen transfer).



Figure 3. Conversion, product yield and mass balance over 6-10 h continuous flow hydrogen transfer at 0.2 mL min⁻¹ using 0.1 M furfural in *i*-PrOH at 230 $^{\circ}$ C and 30 bars using 110 mg of (a) 5%Ni/AC, (b) 10%Ni/AC, (c) 5%Ni-15%W/AC and (d) 10%Ni-15%W/AC.

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All the results observed in continuous flow are in line with the findings reported by Gilkey et al., who demonstrated experimentally the importance of the co-existence of a Lewis acid site in the vicinity of a reduced metal phase in bimetallic systems to accomplish the actual hydrogenolysis of the C-O bonds in FA and who demonstrated the competitive formation of MF (hydrogenolysis product) and 2-(isopropoxy)methylfuran (etherification product).^[20] When the same catalyst was used in the presence of H₂, in similar continuous flow equipment, side product formation still occurred (for details see Figure S2 in the Supporting Information). The products shifted to lower retention times when using ethanol or methanol instead of isopropanol. Moreover, side product formation was fully suppressed (100 % mass balance) by using aprotic polar solvents such as ethyl acetate, methyl isobutyl ketone and methyl cyclopentyl methyl ether, however, with considerable lower activity compared to protic solvents. These results show that side product formation was mostly the result of alcoholysis reactions, which can be catalyzed by acid sites.20,27

Effect of process conditions on catalyst performance. The change in mean crystal size after utilization in batch and continuous flow was compared, as seen from XRD analysis (Figure 4) using the Scherrer equation. A higher crystal size indicates that the metal dispersion is affected negatively (when no metal leaching occurs). In general no drastic effects were observed, except for the crystal size of the Ni(0) phase after utilization at 260 °C, either in batch or in continuous flow (11.2-11.8 nm vs. 6.8-7.8 nm). This effect can be the result of metal nanoparticle aggregation, metal leaching (removal of smallest Ni nanoparticles) or transition to another Ni phase. Note that for the fresh Ni/AC and Ni-W/AC catalysts, much higher crystal sizes were observed when increasing the Ni load from 5 to 10 % in their synthesis, explaining their worse catalytic performance.

The NiO phase was enriched on the catalyst surface (XPS) as well in the bulk catalyst (XRD) after utilization in continuous flow whereas it was not after batch utilization. This effect was caused by the higher leaching of metallic Ni(0) in batch, but additionally phase transition to NiO occurred in continuous flow at 260 °C. Panagiotopoulou and Vlachos obtained high MF yields by inducing a metal oxide (RuO_x) phase along with the metal (Ru) phase by treating catalyst in a posterior oxidation treatment under controlled conditions.^[18] In line with these findings, the results in the present study suggest that the Ni/NiO catalyst was more effective in batch for promoting high MF selectivity whereas the Ni/WOx catalyst in continuous flow (with NiO and WO_x as the Lewis acid sites, respectively). However, as the metal oxide phase was not induced in a controlled way (as it was produced on the carbon surface during storage and also in the bulk carbon under continuous flow conditions), no straightforward conclusions can be drawn on the catalytic contribution of the NiO, WO2 and NiWO4 phases in the Lewis acid-mediated hydride transfer and their capacity to bind hydroxyl groups released in the hydrogenolysis of FA, in addition to the nickel metal-mediated pathway. Although high and stable selectivity to MF was demonstrated for 8 h on stream in continuous flow using bimetallic catalysts, significant metal leaching occurred which decreased the activity. Advanced kinetic studies and further insights in the catalytic role of the individual NiO, WO_2 and NiWO₄ phases may explain better the highly different catalytic performance when moving from batch to continuous flow conditions. Finally, batch processes deal with diffusion mass transfer limitations. The poorer porosity characteristics of the bimetallic Ni-W catalysts may also explain their worse performance in batch conditions (as compared to monometallic Ni).

The fresh mono- and bimetallic catalysts and the corresponding used catalysts were also analyzed with XPS (Figure 5) and ICP-MS to study the extent of metal leaching from the support. The results (Table 3) show the relative elemental composition on the surface (XPS) and in the whole catalyst material (ICP-MS). Interestingly, the XPS analysis of the fresh catalysts showed that the catalyst surface was enriched in metal oxide phase (NiO), especially in the Ni-W catalysts (Table 3, entry 6). In the XRD analysis only low intensity peaks for NiO were observed. This means that a NiO phase had formed on the surface, which is not surprising as the catalysts were stored under air atmosphere. The general trend in the results was that significant metal leaching had occurred (ICP-MS). The leaching effect was substantially higher in batch (40-44 %) than in continuous flow (5-26 %) conditions. This was especially the case for the bimetallic catalyst, from which most of the metal phases, including Ni(0), NiO, WO2 and NiWO4, were leached after utilization in batch.



Figure 4. Crystal sizes of fresh and used mono- and bimetallic Ni catalysts based on XRD analysis: (*) for Ni(0) and (\bullet) for NiO (WO₂ and NiWO₄ signals are not indicated here).

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Figure 5. (Left) Full and (Right) zoomed XPS spectra of (a) fresh 5%Ni/AC, (b) used 5%Ni/AC (batch, (c) fresh 5%Ni/15%W/AC and (d) used 5%Ni/15%W/AC catalysts, after 5 h batch in *i*-PrOH at 260 $^{\circ}$ C in the absence of H₂.

Table 3. C, O, Ni and W content as determined by XPS and ICP-MS analysis in fresh and used mono- and bimetallic Ni catalysts.									
Entry	Catalyst	XPS (wt%) ^[a]						ICP-MS (wt%)	
		С	0	NiO	Ni(0)	W	Ni	W	
1	5% Ni/AC, fresh	86.8	12.3	0.5	0.4	-	4.1	-	
2	5%Ni/AC, used (batch, 200 °C, 30 bars H_2)	79.1	20.4	0.3	0.2	-	2.3	-	
3	5%Ni/AC, used (batch, 260 °C, no H ₂)	86.6	12.3	0.6	0.6	-	2.4	-	
5	5%Ni/AC, used (continuous flow, 260 °C, 30 bars, no ${\sf H}_2)$	82.5	16.7	0.7	0.2	-	3.9	-	
6	5%Ni-15%W/AC, fresh	67.4	15.4	0.5	0.1	17.4	4.3	0.1 ^[b]	
7	5%Ni-15%W/AC, used (batch, 260 °C, no H ₂)	75.4	18.8	0.2	0.0	5.6	2.6	0.1 ^[b]	
8	5%Ni-15%W/AC, used (continuous flow, 260 °C, 30 bars, no $H_2)$	69.6	14.3	0.7	0.1	15.4	3.2	0.1 ^[b]	

[a] based on C (1s), O (1s), Ni(0) (2p3/2), NiO (2p3/2) and W(4f) signals. [b] Not quantitative (only small amounts of W were solubilized in the acid digest due to complex formation)

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rpm). Stirring was kept for 1 h before the water was removed in a rotary evaporator. The resulting catalysts were dried overnight at 100 °C and were then calcined at 500 °C for 3 h under N₂ flow (50 mL min⁻¹), followed by treatment at 450 °C for 3 h under H₂ flow (50 mL min⁻¹). The 5%Pd/C catalyst (4.9 wt% Pd) and the Ni Raney catalyst (92% Ni) were provided by Alfa Aesar

Catalyst characterization. Nitrogen (N2) adsorption/desorption analysis was performed at -196 °C for the determination of the specific surface area (multi-point BET method), total pore volume (at P/Po = 0.99), mircopore area by t-plot analysis and pore size distribution (BJH method using adsorption data or DFT analysis) of the samples, which were previously outgassed at 150 °C for 16 h under 5x10-9 Torr vacuum, using Volumetric Sorption Analyzer (Autosorb-1MP, an Automatic Quantachrome). The powder X-ray Diffraction (XRD) experiments were conducted on a Shimadzu X-ray 7000 diffractometer using a Cu Ka X-ray radiation operating at 45 kV and 100 mA; counts were accumulated in the range of 5-75° with 0.02° steps (20) with counting time 2 s per step. The X-ray Photo-emission Spectrometry (XPS) measurements were carried out with a Phi Quantera Scanning X-ray Microprobe instrument (Chevron Energy Technology Company, Richmond, CA, USA) using Al $K\alpha$ (h·v = 1486.7 eV) radiation. The instrument was equipped with a hemispherical energy analyzer with multichannel detection and an energy resolution of 1.1 eV. The catalysts were mounted on doublesticky tape confining an area of ca. 0.8 cm x 0.8 cm. The tape was completely covered by the catalyst powder and the sample surface was carefully smoothed. Spectra were collected for C-1s, O-1s, Ni-2p3 and W-4f photoelectron peaks. Total spectral accumulation times were 100 minutes per analysis area while irradiating with 100 W of X-ray irradiation. The binding energies (BE) were referenced to the C-1s peak (284.8 eV) to account for charging effects. The XPS spectra were deconvoluted using Gaussian/Lorentzian shaped curves and an iterative least square algorithm provided in Phi Multipak software. The peak areas were computed according to the best possible fittings in order to quantify the W and Ni species contents on the catalyst surface. The crystal size of the metal nanoparticles was estimated using the Scherrer equation based on the characteristic peaks (20) at 44.3° for Ni(0) and 43.2° for NiO, 26.1° for WO2 and 31.1° for NiWO4. The metal content of fresh and used catalysts was determined via inductively coupled plasma optical emission mass spectrometry (ICP-MS, Perkin Elmer, NexION 350X) using the corresponding acid digests. Acid digestions were performed with nitric acid in individual N2 pressurized (40 bars) reaction chambers in microwave equipment (Milestone, UltraWave), with the temperature raising during 25 min. until reaching 220 °C, which was hold during 15 min. The total digestion time was 50 min. and the final HNO_3 concentration was 2 %.

Batch experiments. All the experiments were carried out in a 100 mL stainless steel autoclave equipped with a thermocouple and magnetic stirring (800 rpm), as illustrated in Figure S3 (see Supporting Information). First 300 mg of catalyst was added, followed by 25 mmol furfural and 12 mmol n-octane (external standard IS) dissolved in 60 mL isopropanol (*i*-PrOH). After 3 times purging, 30 bars of H₂ was added. The reaction mixture was stirred and heated to 200 °C (60 bars total pressure). The target temperature was reached after ca. 35-50 min. at which time was set to zero. Additional experiments were carried out without the addition of H₂, both at 200 °C (30 bars total pressure) and 260 °C (92 bars total pressure). After the reaction, the stirring was stopped and the autoclave was cooled in an ice-batch until reaching a temperature below 35 °C before opening the lit. Around 2 mL was taken from the reaction mixture under stirring, from which 1 mL aliquots were analysed after filtration on a 0.22 μm syringe filter. The catalyst was recovered by simple filtration on paper, washing with ethanol (0.5 h) and

Conclusions

A wide range of chemicals can be produced through catalytic hydrogenation of biomass derived furfural. The production of 2methylfuran (MF) in particular is attractive, but high yields were reported only in few cases, as it requires higher temperature and longer reaction time to break the C-O bond in furfuryl alcohol (FA) being the primary product in the reaction pathway. Whereas molecular hydrogen (H₂) is mostly used as the reductant, few studies demonstrated the catalytic hydrogen transfer from alcohols to furfural in the absence of H₂. This catalytic system is not only different from a techno-economic point of view, but also because this way Lewis acids can also take part in the reaction mechanism in addition to the metalmediated hydride transfer, taking into account that strong adsorptive competition exists on the metallic sites. The present study reports the catalytic transfer hydrogenation of furfural in isopropanol at 200-260 °C using monometallic nickel (5%Ni and 10%Ni) and bimetallic nickel-tungsten (5%Ni-15%W and 10%Ni-15%W) catalysts supported on micro/mesoporous activated carbon (AC), resulting in mainly FA, MF and side products, originating from furfural and furfuryl alcohol alcoholysis and polymerization reactions. High furfural conversion (85%) and selectivity to MF (78 %) was obtained with 5%Ni/AC using 30 bars H₂ in batch at 200 °C. In comparison, higher conversion (95 %) was achieved through catalytic hydrogen transfer at 260 °C (without H_2), however with lower selectivity to MF (53 %). The bimetallic Ni-W catalysts resulted in lower conversion and selectivity to MF. In continuous flow, in contrast, the bimetallic Ni-W catalysts performed better than the monometallic Ni catalysts, as they showed to be very selective to MF (> 90 %), however with lower stability than the monometallic catalysts. The selectivity to MF was inversely correlated with the yield to side products. XPS and ICP-MS analysis of fresh and used catalysts showed that significant metal leaching occurred, especially in batch conditions. XPS analysis showed that a substantial amount of a nickel oxide (NiO) phase co-existed with metallic nickel (Ni(0)) on the surface of the fresh catalyst and that phase transition from Ni(0) to NiO occurred under continuous flow, which also may have promoted high selectivity to MF.

Experimental Section

Reagents. See Supporting Information.

Catalyst synthesis. The monometallic (5%Ni/AC and 10%Ni/AC) and the bimetallic (5%Ni-15%W/AC and 10%Ni-15%W/AC) catalysts were prepared by the classic wet impregnation method. First, Norit® SX-Plus carbon was thermally treated at 500 °C under N₂ flow for 3 h (activated carbon, AC). In a typical preparation procedure, the required amount of the metal salt precursor ((NH₄)₆H₂W₁₂O₄₀.xH₂O and/or Ni(NO₃)₂.6H₂O), was dissolved in 20 mL of deionized water and the solution was added dropwise to a suspension of 10 g AC in 100 mL water under stirring (300

drying at 100 $^{\circ}\text{C}.$ All results (conversion and selectivity) are expressed as molar percentages.

Continuous flow experiments. The experiments were conducted without the addition of molecular hydrogen (H₂) in a high-temperature high-pressure Phoenix Flow Reactor (ThalesNano[™], Hungary, see Figure S4), connected to a HPLC pump to supply a continuous feed of a 0.1-0.2 M furfural feedstock in i-PrOH. A 30 mm CatCart cartridge (0.88 mL empty volume) was packed with 110 mg catalyst and placed in the reactor module. The total flow through volume (including feed, reactor and product sections) was 14.0 mL. First, pure i-PrOH was pumped through the system and then the feed was changed to the furfural feedstock. The flow was continued until the temperature (200-260 °C) and pressurization (0-70 bars) of the reactor module were reached. Then, in function of the flow rate (0.1-0.4 mL min-1), the reaction proceeded during a certain time (20-80 min.) before collecting the first sample (sample at time = 0 min). Further samples were collected after regular time intervals (20-40 min). All results (conversion and selectivity) are expressed as molar percentages.

Product analysis. The concentrations of furfural and hydrogenation products were determined by GC-FID. First, calibration curves for furfural, furfuryl alcohol (FA), tetrahydrofurfuryl alcohol THFA, 2-methylfuran (MF) and 2-methyltetrahydrofuran (MTHF) were determined in the 0-25 mg mL⁻¹ range and using *n*-octane (8.1 mg mL⁻¹) as the internal standard for the products obtained in batch experiments (Figure S5), and in the 0-40 mg mL⁻¹ range and using *n*-octane (3.0 mg mL⁻¹) as the internal standard for the products obtained in continuous flow experiments (Figure S6). For the batch experiments, GC-FID analysis was performed on a AutoSystem XL gas chromatograph (PerkinElmer, Norwalk, CT 06859, United States) coupled with a FID detector equipped with a AT™-1HT GC CAPILLARY COLUMNS (30m × 0.25mm i.d. and 0.1 µm film thickness; Alltech Part No.16368). N2 was used as carrier gas at a rate of 1 mL min⁻¹. The samples were injected with an auto-injector directly onto the column using septum-equipped programmable injector (SPI) system in split mode (20.8:1 ratio). The temperature of the injector was set 350 °C and the oven started at 50 °C, held for 6 min, raised to 130°C at a rate of 10°C min⁻¹ and then raised to 250°C at a rate of 30°C min⁻¹ and held for 2 min at 250 °C. The ionisation mode was FID (70 eV, 300 μ A, 300 °C). For the continuous flow experiments, the GC-FID analysis was performed on a gas chromatograph (HP, 14009 Arcade, New York, United States) coupled with a FID detector equipped with a Supelco 2-8047-U capillary column (60 m x 25 m x 25 µm, Alltech Part No.31163-01). N_2 was used as carrier gas at a rate of 1 mL min $^{\text{-}1}$. The temperature of the injector was set 250 °C and the oven started at 80 °C, held for 5 min, raised to 100°C at a rate of 10°C min⁻¹, held for 5 min. and then raised to 120°C at a rate of 10°C min⁻¹ and held for 10 min at 120 °C. The ionization mode was FID (70 eV, 300 $\mu A,$ 250 °C). The identification of the compounds was performed by comparison of the retention times with pure standards. The furfural conversion, the yield and selectivity to each hydrogenation product (Pn) and the corresponding mass balance in batch experiments were calculated as the following:



The amount of moles was calculated from the corresponding concentration (mg mL⁻¹), the molecular weight (g mol⁻¹) and the reaction volume in batch experiments (64 mL).

The furfural (F) conversion, the selectivity and the yield of each hydrogenation product (P) in the continuous flow experiments were calculated as the following:

CF and CP are the concentrations of furfural and hydrogenation product (mol mL^{-1}). The total volume in the system of the continuous flow experiments was assumed to remain constant during the experiments (no evaporation loss).

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Mono- and bimetallic nickel-based catalysts are compared in batch- and continuous flow mode for the catalytic transfer hydrogenation of furfural in isopropanol. The catalytic performance depends mostly on the reactions conditions.

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Batch vs. continuous flow performance of supported monoand bimetallic nickel catalysts for catalytic transfer hydrogenation of furfural in isopropanol

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