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Insights into the activity, selectivity and stability of heterogeneous catalysts in the continuous flow hydroconversion of furfural

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Abstract

The continuous flow hydroconversion of furfural to a range of furanic derivatives was carried out using a range of metal-containing heterogeneous catalysts in order to provide insights into reaction pathways for the hydrogenation of furfural. Most catalysts provided excellent furfural conversion (>60%) and varying selectivities to products at mild temperatures (90ºC) including furfuryl alcohol (FA) 2-methyl furan (2-MF), 2-methyl tetrahydrofuran (2-MTHF) and intermediate furanics depending on the flow conditions and the investigated catalyst.

Keywords: furfural conversion, flow chemistry, hydrogenation, heterogeneous catalysis

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Introduction

The complexity and recalcitrance of biomass (e.g. lignocellulosics) often entails a number of challenges to address and solve to facilitate working with such highly abundant and attractive feedstock in the future. Additional advantages of biomass as resource for the production of high added value chemicals[1] fuels and materials[2, 3]include the presence of highly functionalised compounds containing O and N as well as the potential use of known processing strategies (e.g. hydrodeoxygenation, fermentation, etc.) for valorisation. To better understand pathways and reactivity of biomass, the conversion of biomass-derived platform molecules to useful end products attracted a significant deal of research efforts in the past few years. As example, the hemicellulosic fraction of biomass is enriched in C5 sugars reported to be converted to an useful platform chemical such as furfural via simple xylose dehydration under mild reaction conditions[4, 5].

Furfural is a highly useful chemical intermediate that can be further transformed into several valuable compounds including cyclopentanone (CPO), furfural alcohol (FA)**,** 2-methyltetrahydrofuran (2-MTHF), and 2-methylfuran (2-MF).[6] Various reports have recently investigated a number of homogeneous and heterogeneous catalytic systems for the hydroconversion of furfural into different high added value chemicals and fuel precursors[7]. However, without a few exceptions,[8] these generally provided little insights into reaction pathways and mechanisms and/or a comparison between different commercial catalytic systems (i.e. noble *vs* transition metals; homogeneous *vs* heterogeneous) to propose some general guidelines on furfural conversion and selectivities as well as catalyst stability under continuous flow liquid phase conditions to advance in this important topic in view of the future direct conversion of hemicellulosic feedstocks to furanic compounds. From various contributions on

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mechanistic insights, results provided by Sithisa *et al.* on the conversion of furfural on Pd/SiO_2 and $Pd-Cu/SiO_2$ catalysts most interestingly pointed to a preferential furfural decarbonylation on Pd sites while the addition of Cu rendered a most active hydrogenation catalyst for FA production with a low decarbonylation rate.[8a] Nevertheless, most body of work in the field includes both batch and/or catalytic transfer or vapor phase furfural hydroconversion processes at moderate to high temperatures of low practicality and applicability.

In this sense, we have previously demonstrated that continuous flow processes could provide several relevant advantages in studies related to the conversion of biomass-platform molecules to high added value chemicals (e.g. levulinic acid to gamma-valerolactone and 2-MTHF)[9]. These included the possibility to follow reaction pathways and even fine-tuning reactivity for a number of transition and noble metal heterogeneous catalysts to direct the conversion of levulinic acid to pentanoic acid or alternatively to 2-MTHF.[9] Most importantly, the stability of the catalysts under typical biomass conversion conditions (i.e. aqueous solution, moderate to high temperatures, presence of acid, etc.) could be tested as well as metal leaching into the reaction mixture, one of the most common reasons for catalyst deactivation.[10]

Based on these premises, this contribution was aimed to provide a number of insights into reactivity pathways, deactivation and stability of a number of heterogeneous catalysts in the continuous flow liquid phase hydroconversion of furfural at low temperatures (< 100°C). Different reaction conditions were screened and optimised for which times of reaction, selectivity to products and catalyst stability were tested in view of a potential translation of optimized results to the conversion of furanic waste streams.

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Experimental

Reactions were conducted in an H-Cube mini flow hydrogenation instrument from ThalesNano (Figure 1). A 0.2 M furfural solution in ethyl acetate was prepared using furfural (0.83 mL furfural in 50 mL ethyl acetate) as starting material. The solution is filtered off prior to flowing it through the system to avoid the presence of any undissolved species. The system starts with pumping a solution of pure methanol as washing solvent (0.3 mL min^{-1}, 15 min) through system. Subsequently, methanol is changed to the solvent used in the reaction, in this case ethyl acetate (0.3 mL min^{-1}, 10 min) and the system is set to the desired reaction temperature (90 ºC) and hydrogen pressure (50 bar), as optimum reaction conditions. When the desired parameters are achieved, a 0.2 M furfural solution is pumped through the system in order to carry out the continuous flow hydroconversion of furfural. As the reaction is running, several samples were taken at different times for subsequent analysis and check the catalyst deactivation in the time under the investigated reaction conditions. At the end of the continuous flow process, the system is again switched to ethyl acetate (0.3 mL min^{-1}, 10 min) in order to remove unreacted furfural species or different products of reaction and the reaction parameters (temperature and pressure) are switched off. Eventually, the system is washed again with methanol (0.3 mL min^{-1}, 20 min). Based on the dead volume of the reactor, 20 min of reaction is equivalent to approximately 60 seconds (1 min) of residence time of the furfural solution in the catalyst.

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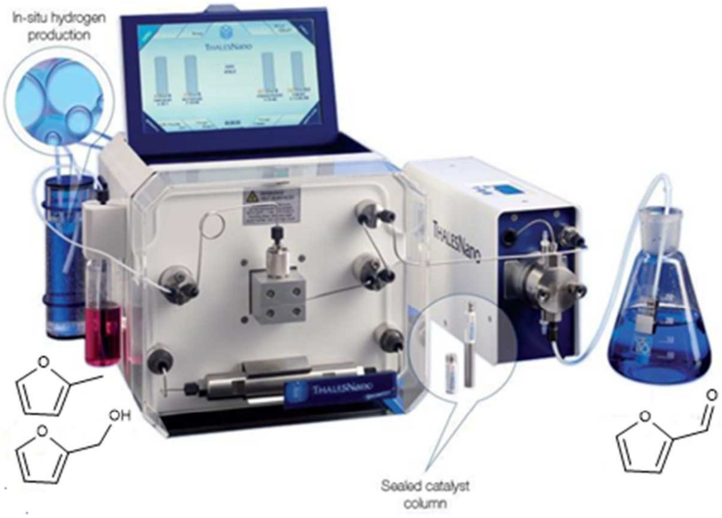

Figure 1. Flow hydroconversion of furfural using the H-Cube mini system.

The continuous flow hydroconversion of furfural was conducted by passing hydrogen generated *in-situ* in the H-Cube equipment from water electrolysis and the flow solution through a packed column containing different solid catalysts (CatCart®) as illustrated in Figure 2.

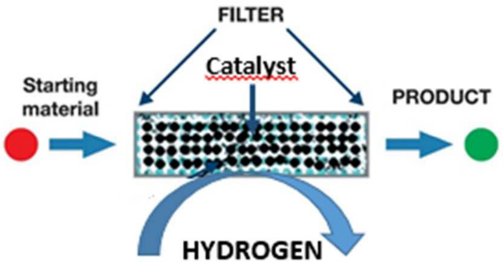

Figure 2. Continuous flow conversion of furfural (starting material) to products over a packed bed of heterogeneous catalyst in the H-Cube mini.

A range of different heterogeneous catalysts were investigated, namely commercial catalytic noble metal/type systems (5% and 10%Pd/C, 10%Pd/PBSAC,

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5%Ru/C and Ru-Sn/Al_2O_3) as well as related transition metal catalysts including, Co/Raney, CuO/Al_2O_3 and a nickel on silica-alumina (NiSiAl) catalyst.

10% Pd-PBSAC was provided by SARATECH® Blucher technologies where PBSAC stands for SATARECH Polymer based Spherical Activated Carbon (monodispersed spheres, 75 μm average diameter, >95% carbon content, with average Pd particle sizes < 5 nm). 5 and 10% Pd/C materials as well as 5% Ru/C were obtained from Alfa Aesar. 5% Pd/C contained 4.93 wt% Pd with a metal area of 20 m^2 g^{-1}, while 10% Pd/C contained a 9.87 wt% Pd and a similar 18 m^2 g^{-1} metal area as compared to 5% Ru/C containing a 4.85 wt% Ru. Ru-Sn on alumina (Ru-Sn/Al_2O_3) powder was a development catalyst from Johnson Mathey containing ca. 5% Ru and Sn low quantities of Sn as promoter.

Co/Raney corresponds to Sponge Cobalt A8B46 promoted with Nickel and Chromium catalyst from Alfa Aesar, containing 1.95% Cr, 2.42% Al, 3.79% Ni and 91.3% Co as measured by ICP (black solid). Cu (II) oxide on alumina is commercial 417971 product (CAS 1317-38-0) from Sigma Aldrich, containing ca. 9-11 wt% Cu, similar to that of 10%Pd systems. Nickel on silica-alumina catalyst (Alfa Aesar) contained a 63.3% Ni, with a 41.6% nickel reduction. Comparatively, Ni/Raney was also commercial from Alfa Aesar with a 92% Ni.

All catalysts were packed by ThalesNano (weight of material packed ca. 0.2 g per cartdrige) in 30 mm long catcarts compatible with the H-Cube system. Optimised reaction conditions included 90ºC, 50 bar hydrogen, flow rate 0.3 mL min^{-1}, 0.2 M furfural solution in ethyl acetate. The furfural solution (brownish) gradually turns into colourless in the course of the reaction.

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Collected samples were analyzed by GC and GC MS using an Agilent 5890N fitted with a SUPELCO EQUITY TM-1 fused silica capillary column (60 m × 0.25 mm × 0.25 μm) and a flame ionisation detector (FID). The identity of the products was confirmed by GC MS at the SCAI of Universidad de Cordoba. The experimental error in all data provided is within typical GC errors (ca. 5-10%) and carbon balances of all reactions conducted in this work are > 95%.

Results and discussion

Continuous flow hydrogenations were conducted under optimised reaction conditions for the selective catalytic systems. These reaction conditions were selected as generally moderate to low conversions were obtained at lower temperatures (<90ºC), higher flow rates (>0.5 mL min^{-1}) and/or reduced hydrogen pressures (below 30-40 bar). Figure 3 demonstrates that good to excellent catalytic activities were achieved for all systems at 90^{o}C and very short residence times (typically 20 min reaction, residence time ca. 1 min). Most interestingly, the continuous flow methodology could provide relevant insights into the activity, selectivity and stability of the different investigated systems.

To begin with, a remarkable difference in terms of activity was observed for noble metal systems as compared to that of transition metal catalysts (Figure 3). As expected, all transition metal systems could provide maximum furfural conversions of ca. 60-70%, with a very low catalytic activity observed for CuO/Al_2O_3. Comparably, quantitative conversion (>97%) was obtained for Pd and Ru systems with the exception of $Ru\text{-}Sn/Al_2O_3$ which will be discussed separately. Generally speaking, selectivities ranged from good to excellent to a single product which varied depending on the

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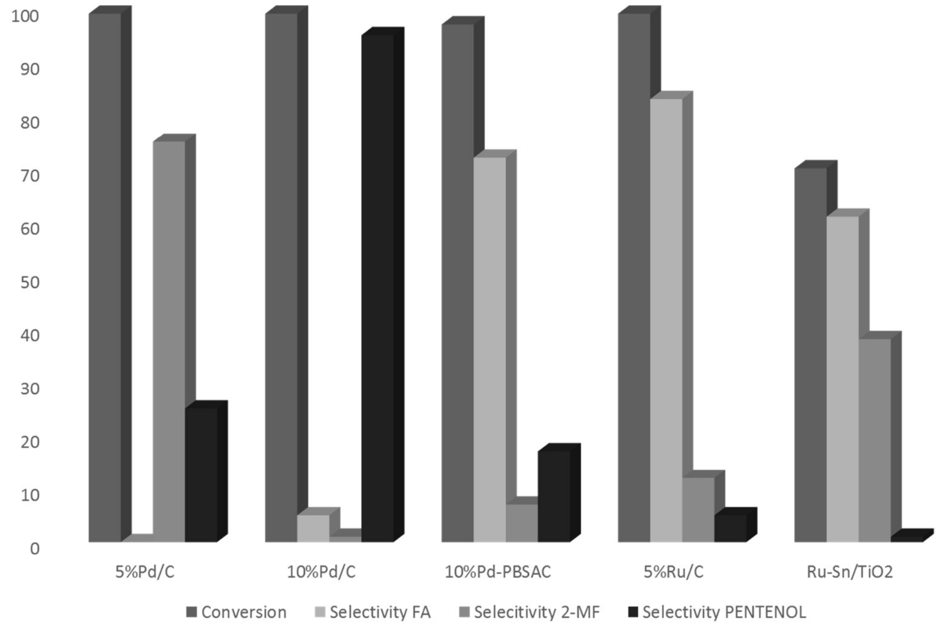
catalyst. Four main products were exclusively observed in all catalytic runs under the investigated conditions, namely furfuryl alcohol (FA), 2-methylfuran (2-MF), 2-MTHF and pent-3-en-1-ol (PENTENOL), an intermediate from 2-MF hydroconversion (Scheme 1). The reaction pathways identified for the different catalytic systems in the continuous flow hydroconversion of furfural under the investigated conditions are highlighted in Scheme 1.

Starting from noble metal systems, a generally high FA selectivity was observed for 5%Ru/C catalysts, in good agreement with previous literature reports.[11] Further hydroconverted products were observed in low selectivities in the reaction using these catalysts including 2-MF and even 2-MTHF. Interestingly, Pd/C systems provided a remarkably different product selectivity under the investigated conditions, with 2-MF and interestingly pent-3-en-1-ol (only for high loaded 10%Pd/C) as major products at quantitative conversion. Comparably, FA was mostly obtained for 10%Pd/PBSAC, with some quantities of linear enols as major side products.



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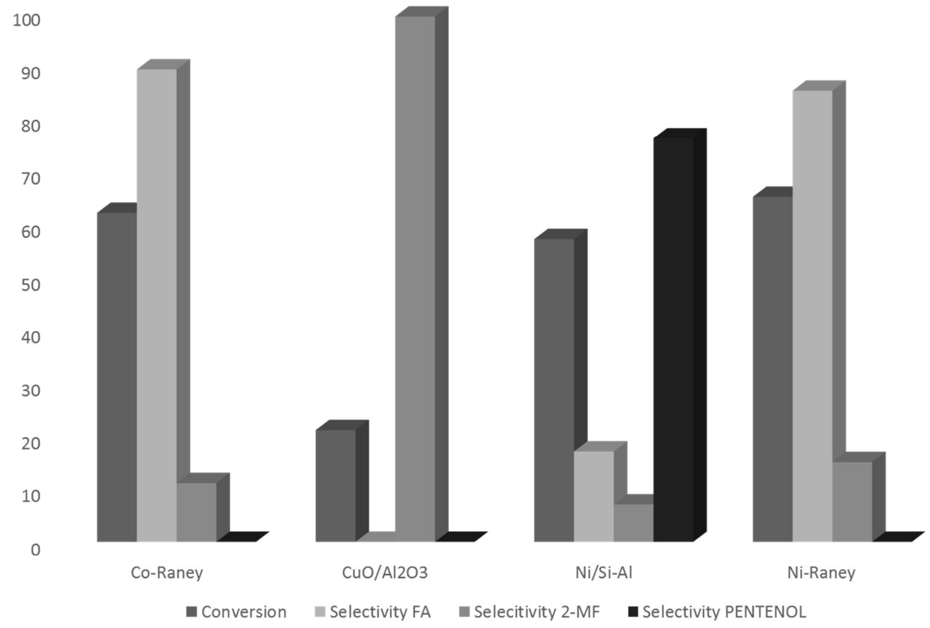

Figure 3. Comparative performance of noble metal (top plot) and transition metal (bottom plot) heterogeneous catalysts in the conversion of furfural under continuous flow. Reaction conditions: 0.2 M furfural in ethyl acetate, 90^{o}C, 50 bar hydrogen, H-Cube-mini, 0.3 mL min^{-1} flow rate, 0.2 g packed catalyst, 20 min on stream (ca. 1 min residence time).

With regards to Pd catalysts, a strong adsorption of furfural on Pd surfaces has been previously [8a]. Such adsorption normally takes place through the aldehyde group which leads to a stepwise hydrogenation/hydrogenolytic conversion of furfural into FA and eventually 2-MF, proposed to be related to an interaction of Pd with both C and O atoms of the carbonyl group which generate stable acyl surface species as precursor of decarbonylation.[8a] Our results are in good agreement with such data despite the relatively low temperature of our studies. The presence of the methyl group in 2-MF may favor cleavage through the C-O bond giving rise to linear dienes as illustrated in Scheme 1.

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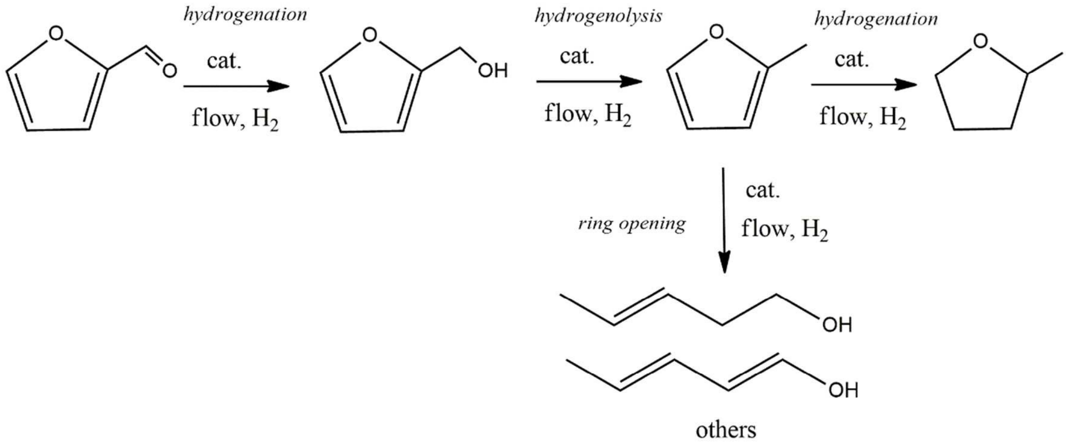

Scheme 1. Reaction products and intermediates obtained in the continuous flow hydroconversion of furfural using heterogeneous catalysts.

Most importantly, the nature of Pd species found in both the fresh and used Pd/C commercial catalysts seem to support these findings as shown in Figure 4. XPS studies of fresh Pd/C (both 5 and 10%) indicated a majority of Pd (II) content in the materials, with a minor proportion (<20%) of Pd (0) as depicted in Figure 4, top spectra. The presence of Pd (II) species can promote hydrogenolytic cleavage at low temperatures[12] (FA to 2-MF and further to pentenols), with the comparably low Pd (0) species promoting the subsequent partial hydrogenation of the diene upon formation.[8, 12]. Interestingly, hydroxy-containing dienes were also detected in traces in all Pd containing systems (also for 5%Pd/C) which seem to correlate well with the proposed reaction mechanism and current findings. To the best of our knowledge, this is the first example of a Pd-catalysed flow hydroconversion of furfural able to provide quantitative yields of pentenols (>99% conversion, >95% selectivity) under mild reaction temperatures.

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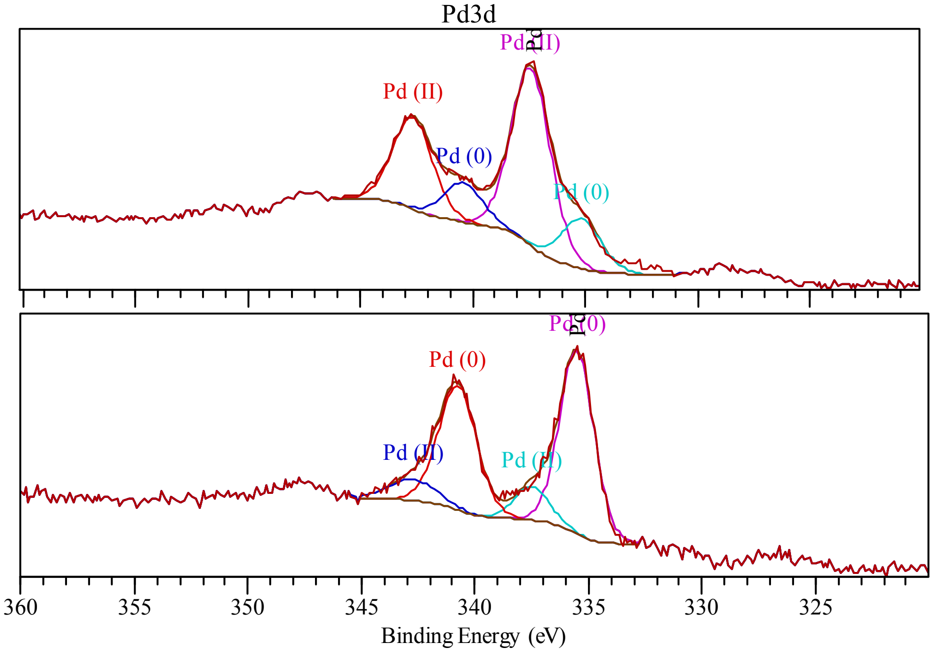

Figure 4. XPS data of 5%Pd/C fresh (before reaction, top spectra) vs 5%Pd/C used (after 2 h on stream, bottom spectra). Clear differences in Pd (II) vs Pd (0) species can be observed for both catalysts.

An interesting behavior was also observed for 5%Pd/C with time on stream. A slight deactivation (>99% to 77-80%) was observed with a remarkable change in selectivity from 2-MF as main product to FA (Figure 5). The deactivation may be due to some nanoparticle sintering as clearly visualized for the case of 5% Pd/C (Figure 6) since negligible Pd leaching (ca. 2% of total Pd content) as measured by XPS (surface Pd) and repeated ICP-MS could be observed in the material with time on stream. Surface areas did not significantly change also in fresh vs deactivated catalysts. Remarkably, the change in selectivity was in fact due to a change in the oxidation state of Pd species with time on stream (Figure 4, bottom spectra). XPS data clearly pointed out that the high hydrogen pressures employed under optimum conditions (50 bar) lead

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to a gradual reduction of Pd (II) species to Pd (0), with a majority of Pd (0) present in 5%Pd/C after 2-4 h on stream (Figure 4 bottom vs Fig 4 top spectra). In the used 5%Pd/C system, Pd (0) species favoured the hydrogenation of the carbonyl group to FA at low temperatures, supporting the reduction in the hydrogenolytic capacity (FA to 2-MF) of the system due to a reduction of Pd (II) to Pd (0) with time of stream under the investigated flow conditions. A similar behavior was also observed for some transition metal systems and even for Ru catalysts, although this selectivity switch was not so evident.

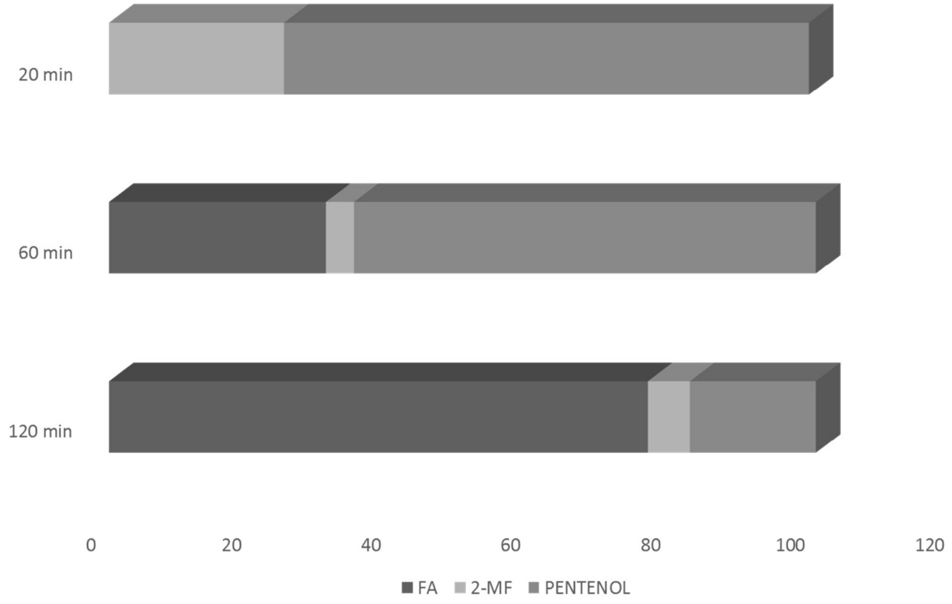

Figure 5. Selectivity evolution with time of reaction for 5%Pd/C in the continuous flow hydroconversion of furfural. Reaction conditions: 0.2 M furfural in ethyl acetate, 90^{o}C, 50 bar hydrogen, H-Cube-mini, 0.3 mL min^{-1} flow rate, 0.2 g packed 5% Pd/C; >99% conversion (20 min reaction, ca. 1 min residence time); 77% conv. (60 min reaction, ca. 3 min residence time); 80% conv. (120 min reaction, ca. 6 min residence time).

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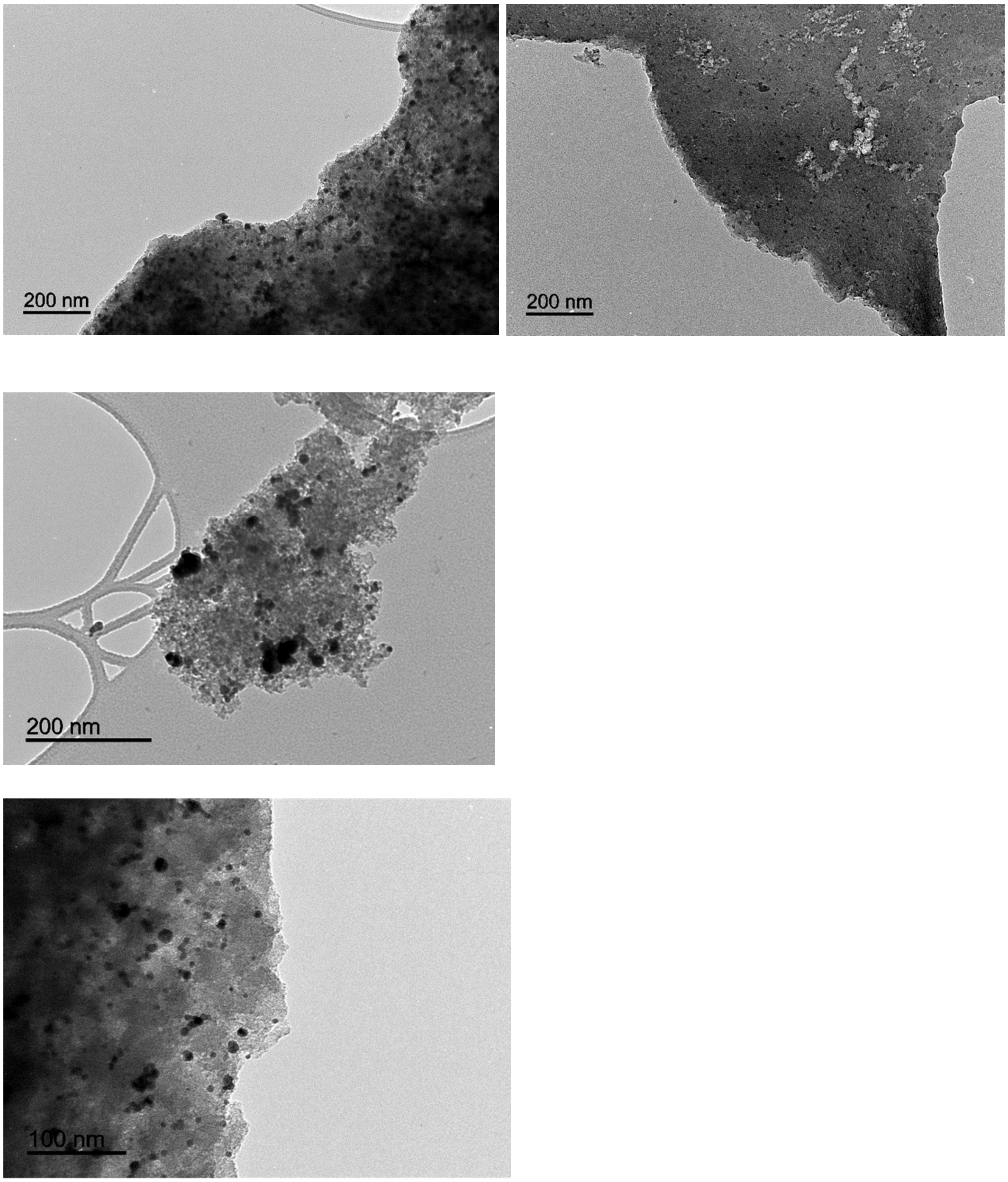

Figure 6. TEM images of 5%Pd/C fresh (top images) and used (after 2 h on stream, bottom images). The presence of large Pd aggregates (>30 nm) can be visualised in the used catalyst, with an also large increase in particle size diameter (average ca.15 nm in size, counting 50 nanoparticles) as compared to the fresh 5%Pd/C (average ca.13 nm in size, counting 50 nanoparticles).

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However, Pd (II) to Pd (0) reduction also evidenced in the case of 10%Pd/C (results not shown) was not driven to a major Pd (0) presence in such commercial catalysts, perhaps due to the higher Pd content, leaving the right balance between Pd (II) species to promote hydrogenolytic cleavage of FA and 2-MF to pentenols and Pd (0) species to promote the subsequent hydrogenation steps.

Last but not least, the stability of the catalysts was investigated under the optimized reaction conditions, pointing to very different trends between noble and transition metal catalysts (Figures 7 to 9). All Pd systems were highly stable under the investigated reaction conditions, with only minor leaching (maximum 5 ppm, 1-5% of total Pd content) observed for all catalysts including 5%Pd/C for which a slight decrease in activity was observed (>99 to 80%, Figure 7). The conversion for 5% Ru/C slightly decreased with time on stream (from >98 to 85%, due to metal sintering as in the case of Pd) but no significant leaching was also detected.

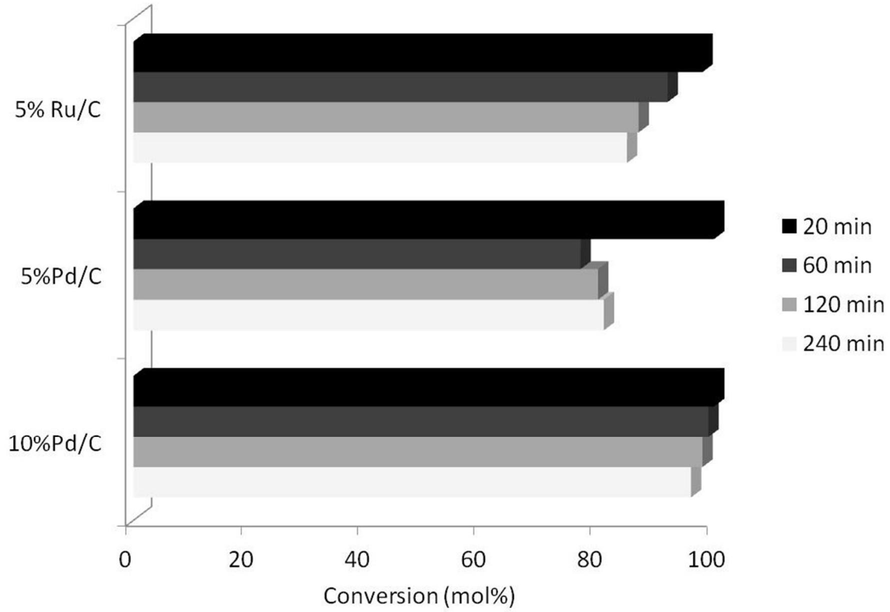

Figure 7. Evolution of conversion of noble metal-based catalyst with time on stream. Reaction conditions: 0.2 M furfural in ethyl acetate, 90^{o}C, 50 bar hydrogen,

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H-Cube-mini, 0.3 mL min^{-1} flow rate, 0.2 g packed catalyst. 20 min time on stream is equivalent to ca. 1 min residence time, hence residence times ranged from 1 to 12 minutes.

Comparably, all transition metal systems significantly deactivated under the investigated reaction conditions, with the exception of CuO/Al_2O_3 which in any case provided low conversion (15-20%) in the flow experiments. No further leaching/stability studies were conducted with such catalysts due to their low stability under the investigated continuous flow conditions but preliminary tests indicated a combination of both metal sintering and leaching. High selectivities to FA were obtained for all transition metal catalysts regardless of deactivation issues. Of interest was the high selectivity of CuO/Al_2O_3 to 2-MF and especially 2-MTHF in time despite the mild reaction conditions (Figure 7). These findings were in good agreement with previous work of the group in the hydroconversion of levulinic acid for which CuO/Al_2O_3 provided excellent activities and selectivity to 2-MTHF.[9] A further investigation on the Cu catalyst indicated the presence of Cu (II) species as pointed out in XPS experiments might be responsible of the observed behavior (results not shown) but further investigations are needed in this point. Literature data seem to contradict these findings, with C-O hydrogenolysis dominating at high temperatures (due to high activation required) as opposed to furfural hydrogenation taking place at low temperatures.[8a, 13] No further studies were performed to ascertain such different behavior due to the low conversion and stability observed for Cu systems under continuous flow liquid phase conditions.

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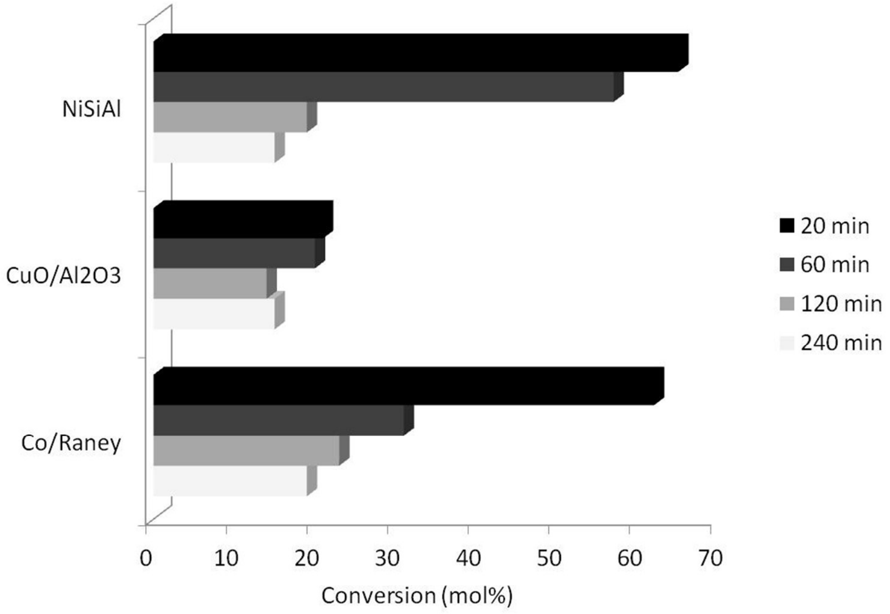

Figure 8. Evolution of conversion of transition metal-based catalyst with time of reaction. Reaction conditions: 0.2 M furfural in ethyl acetate, 90^{o}C, 50 bar hydrogen, H-Cube-mini, 0.3 mL min^{-1} flow rate, 0.2 g packed catalyst. 20 min time on stream is equivalent to ca. 1 min residence time, hence residence times ranged from 1 to 12 minutes.

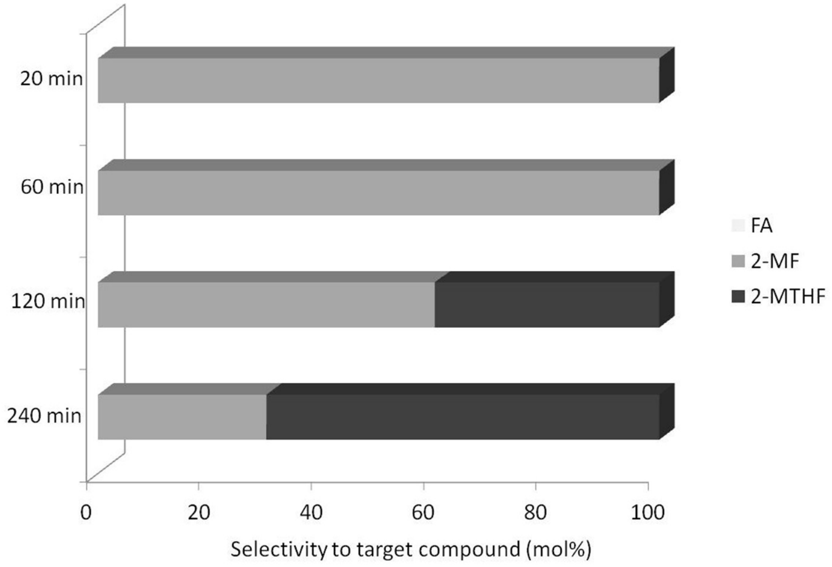

Figure 9. Evolution of selectivity of CuO/Al_2O_3 with time on stream in the hydroconversion of furfural. Reaction conditions: 0.2 M furfural in ethyl acetate, 90°C, 50 bar hydrogen, H-Cube-mini, 0.3 mL min^{-1} flow rate, 0.2 g packed CuO/Al_2O_3. 20 min time on stream is equivalent to ca. 1 min residence time, hence residence times ranged from 1 to 12 minutes.

Conclusions

The proposed studies clearly demonstrated the significance and potential of continuous flow processes for the conversion of platform molecules to useful chemicals, providing the additional possibility to find out stable and highly active heterogeneous catalytic systems for further work with actual biomass feedstocks (i.e. hemicelluloses). Pd catalysts provided optimum results in the flow conversion of furfural to 2-MF and even pentenols, with promising insights into mechanistic aspects and deactivation pathways depending on Pd loading (5-10%) and essentially oxidation states of Pd species in the catalyst, with respect to 5%Ru/C as optimum alternative for high yields of FA. Comparably, transition metal catalysts were proved of low significance in the flow hydroconversion of furfural under the investigated conditions, with moderate yields and varying selectivity to products (mostly to FA) and prone to deactivation with time on stream. We envisage the current findings to be able to pave the way to the design of more stable designer catalytic systems for the continuous flow hydroconversion of other platform chemicals (e.g. succinic and lactic acids, sorbitol) which will be reported in due course.

Acknowledgments

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