

Microwave-assisted Selective Hydrogenation of Furfural to Furfuryl Alcohol Employing a Green and Noble Metal-free Cu Catalyst

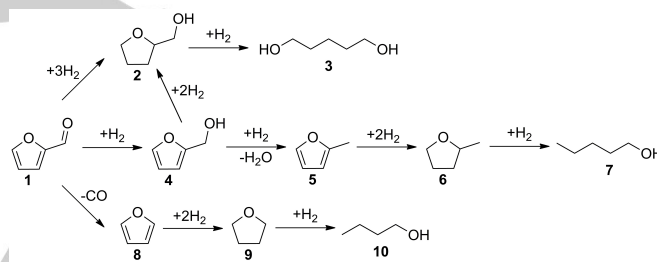
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Abstract: Green, cheap and robust copper-based heterogeneous catalysts afford 100% conversion and 99% selectivity in the conversion of furfural to furfuryl alcohol when using cyclopentyl methyl ether as green solvent and microwave reactors at low H₂ pressures and mild temperatures. The utilization of pressurized microwave reactors produces a 3–4 fold increase in conversion and an unexpected enhancement in selectivity as compared to the reaction carried out at the same conditions using conventional autoclave reactors. The enhancement in catalytic rate produced by microwave irradiation is temperature-dependent. This work highlights that using microwave irradiation in the catalytic hydrogenation of biomass-derived compounds is a very strong tool for biomass upgrade that offers immense potential in a large number of transformations where it could be determinant for commercial exploitation.

Furfural (FAL) has recently gained a lot of attention as a key platform chemical derived from hemi-cellulosic biomass.^[1–2] Furfural hydrogenation may lead to several higher value products, such as furfuryl alcohol (FOL), tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (MF) and 2-methyltetrahydrofuran (MTHF), as depicted in Scheme 1.^[3–5] The development of an adequate catalytic system in order to control the selectivity to a desired product is a critical step that still deserves a lot of attention as much as developing greener and highly active catalysts.

Furfuryl alcohol is an important furan derivative finding application in the production of resins,^[6] as an intermediate for the production of lysine, ascorbic acid and lubricants,^[6–7] as well as a hypergolic fuel in rocketry.^[8] Furfuryl alcohol is currently produced on industrial scale by liquid or vapor phase hydrogenation of furfural employing a copper chromite catalyst, with an annual production of 400,000 t.^[9] The main drawbacks of the current process are: the toxicity of the catalyst used; relatively high pressures of H₂, in case of liquid phase hydrogenation; and high temperatures, meaning high energy consumption for the vapor phase hydrogenation.^[9]

The majority of the scientific papers addressing the production of FOL either use harsh conditions,^[10–17] high pressures of H₂,^[14, 18] or noble metals,^[19–21] which are becoming scarce, more expensive and raise many sustainability concerns. Kyriakou et al. have recently tested Pt nanoparticles supported on γ -Al₂O₃, SiO₂, CeO₂ and ZnO, obtaining 80 % conversion of furfural and 99 % selectivity to FOL after 7 h at 50 °C, using methanol as solvent and Pt/ γ -Al₂O₃ as catalyst.^[7] On the other hand, Jérôme et al. presented a very exciting result with a partly recyclable Co/SBA-15 catalyst, that reaches 88 % yield of FOL after 1.5 h at 150 °C and 20 bar of H₂.^[9] However, the conversion decreased from 92 % to 81 % between the first 2 cycles and continued to decrease slowly in the subsequent cycles. Xie et al. reported a maximum yield of FOL of 90 % after 5 h at 160 °C and 90 bar of H₂ using a Cu-Fe catalyst, which was also active for the hydrogenation of levulinic acid.^[14]



Scheme 1. Main products obtained from furfural hydrogenation and side reactions: furfural (1), tetrahydrofurfuryl alcohol (2), 1,5-pentanediol (3), furfuryl alcohol (4), 2-methylfuran (5), 2-methyltetrahydrofuran (6), 1-pentanol (7), furan (8), tetrahydrofuran (9) and 1-butanol (10).

Cyclopentyl methyl ether (CPME) has emerged in the past few years as a new safer and green solvent alternative to other ether solvents such as, 1,4-dioxane, tetrahydrofuran and methyltetrahydrofuran. This is because it offers low peroxide formation and toxicity, narrower explosion range, high hydrophobicity and stability under acidic and basic conditions, in addition to a relatively high boiling point.^[22–27] Overall, CPME addresses eight of the twelve principles of Green Chemistry.^[28] Therefore, in the present work, CPME was evaluated as a potential green solvent for FOL production yet unexplored for this reaction.

Recently, microwave-assisted reactions have experienced an increase in popularity among the scientific community. Microwave (MW) irradiation enables a fast, uniform and efficient dielectric heating of the reaction media, generating an increase in reaction rates, as well as reducing the energy consumption.^[29–34] The use of the technique represents a breakthrough in terms of sustainability, efficiency, development of new materials and

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cost reduction.^[31, 35-37] To the best of our knowledge, the use of microwave irradiation has never been reported in furfural hydrogenation aiming at producing FOL.

Herein we report a green and efficient catalytic system for the selective hydrogenation of furfural to furfuryl alcohol, that combines a more sustainable, highly active and recyclable catalyst, Cu/TiO₂, with the use of a novel green solvent (CPME) under conventional and microwave heating under H₂ pressure.

The powder x-ray diffraction (PXRD) patterns of the calcined and reduced Cu/TiO₂ catalysts are shown in Figure 1. In the case of the reduced catalyst, it was possible to identify only the diffraction peaks related to the cubic Cu⁰ phase, that is to say, $2\theta = 43.1^\circ$ (111), $2\theta = 50.2^\circ$ (200) and $2\theta = 73.9^\circ$ (220) (JCPDS 00-004-0836). Concerning the calcined sample, only the characteristic peaks of CuO, $2\theta = 35.3^\circ$ (002) and $2\theta = 38.5^\circ$ (111) were observed, as expected (JCPDS 00-048-1548). The rest of the diffractions could be attributed to the anatase (JCPDS 00-021-1272) and rutile (JCPDS 01-075-1748) phase of titania.

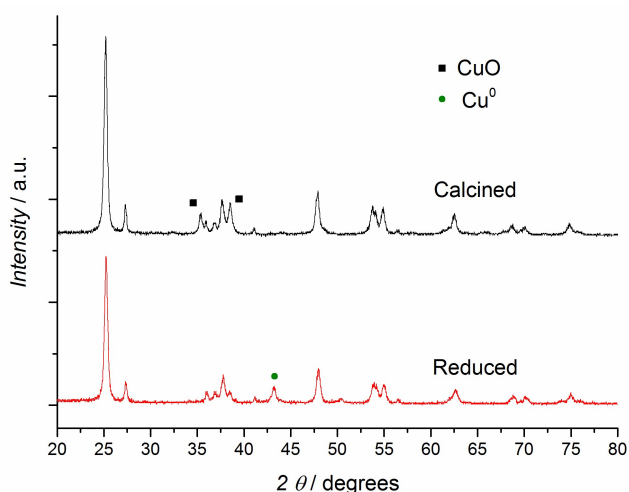


Figure 1. Powder x-ray diffraction of the calcined (black) and reduce (red) Cu/TiO₂ catalyst.

Thermal gravimetric analysis (TGA) was performed to assess the evolution of the decomposition of the copper precursor, as depicted in Figure S.1 of the Supporting Information. The results show that the calcination conditions employed (400 °C, 4 h) were enough to decompose all the copper precursor salt.

In order to evaluate the reducibility of the calcined catalyst, temperature programmed reduction (TPR) analysis with hydrogen was performed and it is displayed in Figure 2. In the case of Cu/TiO₂, two sharp and narrow peaks were observed at 127 and 175 °C. It is common to assign the first reduction peak to the stepwise reduction of Cu²⁺ to Cu¹⁺ whereas the second peak should be related to the reduction of Cu¹⁺ to Cu⁰.^[38-40] However, another possible explanation would rely on the existence of different copper species present on the support. Therefore, the first peak could be due to the reduction of highly dispersed copper nanoparticles while the second could be related to the reduction of bulk copper oxide species or larger particles.^[41-42] Transmission electron microscopy (TEM) of the

freshly reduced Cu/TiO₂ catalyst along with particle size distribution are shown in Figure 3. It is possible to see that the catalyst is comprised of relatively small copper nanoparticles with a narrow size distribution, having an average size of approximately 2.2 nm. Figure S.2 of the Supporting Information shows a TEM image of the TiO₂ support, highlighting the lattice d-spacing corresponding to the (101) plane of the anatase phase.

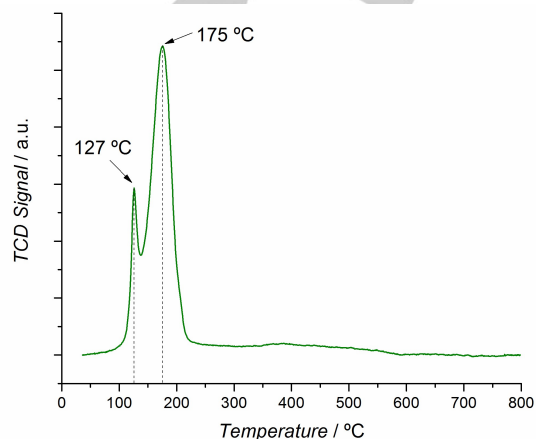


Figure 2. H₂ temperature programmed reduction curve of the calcined Cu/TiO₂ catalyst. Experimental conditions: 5% H₂ in N₂, 50 mL/min, 10 °C/min, 50 mg of sample.

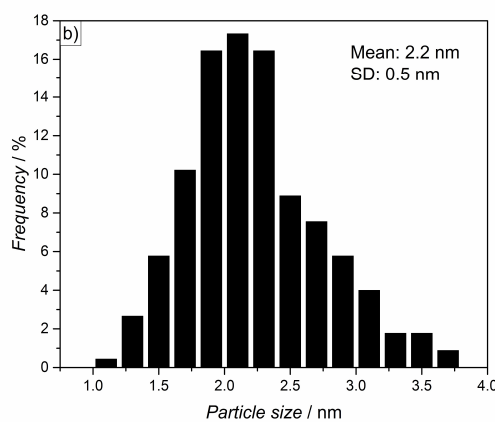
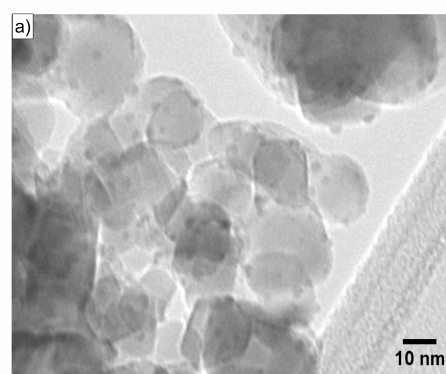


Figure 3. Transmission electron micrograph of freshly reduced Cu/TiO₂ catalyst (a). Particle size distribution for Cu/TiO₂ catalyst (b).

Table 1. Furfural selective hydrogenation to furfuryl alcohol. Experimental conditions: 125 °C, 10 bar of H₂, 10 mg of 10% Cu/TiO₂, 5 mL of a 40 mM FAL solution in CPME. Reactions performed in the MW reactor. [a]

Entry	Reaction time [min]	FAL Conversion [%] ^[b]	FOL Selectivity [%] ^[b]	MF Selectivity [%] ^[b]	FOL Yield [%]	MF Yield [%]
1	20	3	100	0	3	0
2	60	46	100	0	46	0
3	120	97	100	0	97	0
4	180	100	99	1	99	1
5	240	100	99	1	99	1

[a] Reaction without catalyst at the same conditions resulted in a negligible FAL conversion (~1%) [b] Determined by GC.

Catalytic tests were performed with the synthesized Cu/TiO₂ catalyst in a MW reactor at 125 °C and 10 bar of H₂, as depicted in Table 1. The blank test that was done in the absence of catalyst showed a negligible FAL conversion at these conditions. It is possible to see that the catalyst is highly active and highly selective towards FOL, reaching 97 % conversion with 100 % selectivity to FOL in 2 h. Moreover, 99 % yield of FOL was obtained after 3 h with a minor formation of MF due to FOL hydrogenolysis. These are particularly good results considering that low hydrogen pressures and low temperatures were utilized.

It is well known that deactivation of copper based catalysts is one of the major drawbacks for Cu catalysis and it is very often neglected, so after these promising preliminary results, we decided to test the recyclability of the Cu/TiO₂ catalyst. Figure 4 shows the results of the three cycles of recycling tests performed with the Cu/TiO₂ catalyst.

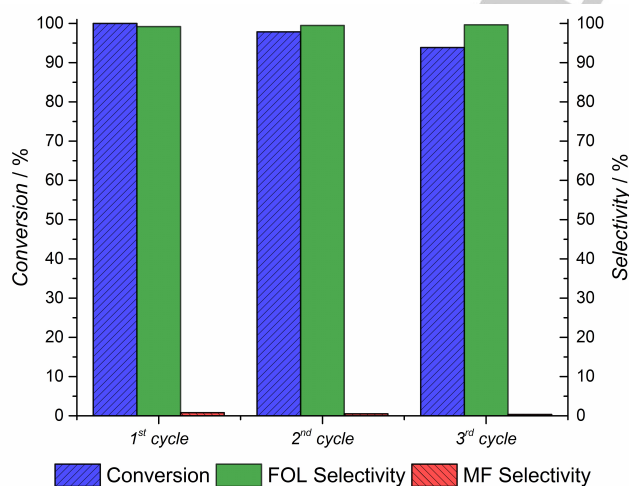


Figure 4. Recycling tests for furfural hydrogenation to furfuryl alcohol over Cu/TiO₂. Experimental conditions: 125 °C; 10 bar of H₂; 180 min; 10 mg of 10% Cu/TiO₂; 5 mL of a 40 mM FAL solution in CPME; MW reactor. Legend: conversion (blue striped bar), furfuryl alcohol selectivity (green bar), 2-methylfuran selectivity (red striped bar).

It is possible to observe that the catalyst is reusable at the tested conditions, with a minor decrease in conversion from 100 % to 94 % after the third reaction cycle, maintaining, however, a high selectivity to FOL. The most common reason for Cu based catalysts deactivation is metal nanoparticle sintering, which reduces the metallic surface area available for catalysis. Concerning the Cu/TiO₂ catalyst, no signs of severe sintering were observed, which we believe is due to an intimate interaction between metal and support (SMSI) [41-42] or an electronic metal-support interaction (EMSI), as proposed by Campbell.[43-44] This interaction would allow the catalyst to retain the majority of its activity, preventing particle sintering. Similar effects have been reported in the literature that we believe support our conclusions for the hydrogenation of furfural under microwave heating with Cu/TiO₂ catalyst.[42, 45-46] In this sense, we attribute the slight decrease in activity between each cycle to a really modest sintering of the Cu nanoparticles or to a minor surface oxidation occurred during the recycling process. The combination of a high activity/selectivity with good stability makes this material a promising catalyst for furfuryl alcohol production from furfural.

Subsequently, we decided to perform an additional set of reactions under conventional heating in an autoclave, at the same conditions employed in the MW studies: 125 °C and 10 bar of H₂. The comparison between the reaction profile with both heating systems is shown in Figure 5.

The differences between the two systems are striking, the reaction carried out under microwave heating presenting a much higher reaction rate, reaching full conversion at 180 min, in contrast to only 35 % conversion under conventional heating. Although microwave reactors have been used for a few years in organic reactions, the real influence and effects that MW irradiation has upon the reaction medium is yet not completely understood and this is particularly complex for reactions catalyzed by solid catalysts.[47-48] The existence of "non-thermal" microwave effects or specific microwave effects is still a very controversial topic and our findings do not show evidence towards a definitive conclusion.[48-50] However, we believe that our results can be explained by means of thermal effects only.[51] Microwaves have the ability, through dielectric heating, to selectively heat specific parts of the reaction medium which may

lead to higher reaction rates and changes in selectivity.^[30, 32, 49] Several authors have observed the formation of hot spots in heterogeneous catalysts during MW irradiation, as a result of the materials' high dielectric constants and loss tangent.^[31-32, 51-52] That could raise the temperature of the active sites of the catalysts locally, higher than the temperature of the bulk and, that alone could explain higher reaction rates.^[31, 47, 51] In accordance to this, titania has a high dielectric constant of ~ 50 , which means that it absorbs MW very well, getting superheated above the solvent bulk temperature.^[47] However, we have not come to an explanation as to how this effect could explain the enhancement in selectivity we observe in Figure 5, as hot spots would typically result in a loss of selectivity. Indeed, the reaction in the microwave is not only faster, but somewhat hinders the consecutive conversion of methyl furfural to methyl furan resulting in almost 100% selectivity. We also know that higher reaction temperatures result in loss of selectivity at isoconversion (Figures S.3 and S.4), and this would suggest that hot spots should have a negative effect on selectivity as well. Interestingly, Holzgrabe et al. have proposed that when hydrogen is adsorbed at the catalyst surface, a dipole moment can be induced which would allow the microwaves to interact with the adsorbed hydrogen.^[52] Although we have no evidence for such phenomena taking place during reaction, we cannot exclude that they are responsible for the unexpected enhancement in selectivity we observe. In any case, the choice of support plays a crucial role in the present case, not only improving the catalyst stability, preventing nanoparticles sintering, but also boosting the reaction rate when coupled with MW irradiation. For practical applications, and despite the very mild temperatures utilized, it is important to stress that the time required to reach the temperature set point in microwave-assisted reactions was usually less than three minutes. In contrast, the reactions under conventional heating took fifteen to twenty minutes to reach the same temperature.

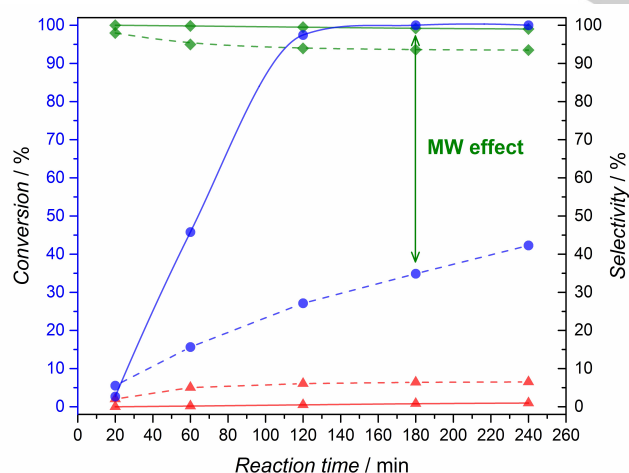


Figure 5. Comparison between furfural hydrogenation over Cu/TiO₂ under conventional heating (dashed lines) and microwave irradiation (solid lines). Legend: conversion (blue line, circle marker), furfuryl alcohol selectivity (green line, diamond marker) and 2-methylfuran selectivity (red line, triangle marker). Parr reactor conditions: 125 °C; 10 bar of H₂; 60 mg of 10% Cu/TiO₂; 30 mL of

a 40 mM FAL solution in CPME. MW reactor conditions: 125 °C; 10 bar of H₂; 10 mg of 10% Cu/TiO₂; 5 mL of a 40 mM FAL solution in CPME.

Moreover, we decided to study the effect of the reaction temperature for both systems. Therefore, we carried out another set of reactions at 150 °C (Figure S.3) and 175 °C (Figure S.4) at 10 bar of H₂ under conventional and MW heating. It is possible to observe, in Figure S.3, that the disparities between reaction rates of the two systems at 150 °C are less pronounced when compared to the reactions performed at 125 °C. Surprisingly, at 175 °C (Figure S.4) no significant differences in conversion and selectivities were observed. A possible explanation of this fact could still rely on thermal effects due to the metal/support superheating. At low temperatures, the reactions proceed slowly due to energy limitations, so when MW irradiation is employed hot spots generate localized higher temperatures in the metal and support, therefore enhancing the reaction rate. At higher temperatures, the microwave heating effect is attenuated, as the available energy starts to be high enough to quickly convert the molecules, gradually decreasing the differences between both systems until no significant MW effect is noticeable.

In conclusion, we have shown that a simple impregnation method provides a cheap, active, stable and sustainable catalyst (Cu/TiO₂), that works at low temperatures (125 °C) and low H₂ pressures (10 bar of H₂) for the FAL hydrogenation to FOL. High yields of FOL were achieved (>99 %), employing CPME as a promising novel green solvent for hydrogenation reactions. In addition, we have assessed and compared the differences regarding the reaction evolution under conventional heating and MW irradiation at different temperatures. We have observed much higher reaction rates under MW irradiation at mild temperatures, which are temperature dependent and could be explained by localized thermal effects. We can conclude that the system composed of Cu/TiO₂ as catalyst, CPME as solvent and MW irradiation as heating source is a promising, efficient and green system for furfuryl alcohol production. Importantly, microwave dielectric heating has the potential to be a great tool, aiming at reducing overall reaction conditions while ensuring high reaction rates for bio-derived reactions. Furthermore, this work is a first example highlighting that using pressurized microwave reactors in the catalytic hydrogenation of biomass-derived compounds can offer huge advantages in terms of conversion and selectivity and, we believe that this offers immense potential in a large number of hydrogenations, but also oxidative transformations where it could be determinant for commercial exploitation.

Experimental Section

Cyclopentyl methyl ether ($\geq 99.9\%$), copper nitrate trihydrate puriss. pa. (99-104 %), were purchased from Sigma-Aldrich. Titanium (IV) oxide, Aerioxide™ P25 was purchased from Fisher Scientific. Reagents were used as received.

The Cu/TiO₂ catalyst was prepared by a simple wet impregnation method. The amount of dissolved Cu(NO₃)₂ precursor was calculated, aiming at achieving a 10 % copper loading. After the impregnation, the catalyst was dried overnight at 100 °C. The Cu/TiO₂ catalyst was

calcined at 400 °C for 4 h under air. After calcination and prior to all catalytic tests, the catalyst was reduced at 400 °C for 4 h under flow of pure H₂.

PXRD patterns were recorded in transmission mode with a PANalytical X'Pert Pro HTS diffractometer with a slit of 0.04° from 2θ = 4 to 90° using a Cu Kα radiation. TPR analyses were performed with a Micromeritics AutoChem II 2920 equipped with a TCD detector. The samples (50 mg) were heated up to 800 °C at 10 °C/min with a flow of 20 mL/min of 5 % H₂ in N₂. TEM characterization was performed using a JEOL JEM 2100 LaB6 instrument at 200 kV accelerating voltage. The samples were sonicated in methanol and supported on holey carbon film on gold grids (300 mesh). Particle size distributions were determined from counting of at least 200 particles.

The reactions performed under conventional heating were carried out in a Parr reactor Series 4590 with a volume of 50 mL. The reactor was loaded with 30 mL of a 40 mM stock solution of furfural in CPME and 60 mg of catalyst. The vessel was then closed, purged five times with nitrogen and heated up to the desired temperature with a stirring of 1,000 rpm. Finally, after reaching the set point temperature, the reactor was pressurized with 10 bar of H₂ and the reaction was considered to start.

A CEM Discover SP microwave reactor was employed in order to perform the microwave-assisted hydrogenation reactions. The reactor was equipped with a gas addition kit containing an in-situ fiber optic temperature control and a 10 mL reaction vessel operable up to 200 °C and 14 bar of pressure. The reactor was loaded with 5 mL of the same stock solution used in the Parr reactor and 10 mg of catalyst. Finally, the vessel was purged five times, loaded with the desired H₂ pressure and heated up with the maximum stirring speed available. The reaction was considered to start as soon as the temperature ramp started and the temperature set point was usually reached in less than three minutes.

The reaction products were identified by GC-MS (Agilent 5975, HP-5ms capillary column) and quantitatively determined by GC (Agilent 7820A) employing a FID detector and a HP-5 capillary column (30 m x 0.32 mm x 0.25 μm). The carrier gas used was nitrogen with a flow of 2 mL/min.

Recycling tests were performed in the following manner: after each reaction, the catalyst was recovered by centrifugation, washed three times with methanol, dried and then recharged in the reactor following the same procedure as described before.

Acknowledgements

The authors are grateful to Dr. Thomas Davies for the TEM analysis at the NiCal (Nano Investigation Centre of Liverpool).

The authors gratefully acknowledge the financial support of CNPq, CAPES-Brazil, EPSRC (grant EP/K014773/1), the UK Department for Business Skills and Innovation (Regional Growth Fund, MicroBioRefinery project) and the Centre for Materials Discovery of University of Liverpool.

Keywords: furfural • furfuryl alcohol • hydrogenation • microwave chemistry • copper

- [1] J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem. Int. Ed. Engl.* **2007**, *46*, 7164-7183; *Angew. Chem.* **2007**, *119*, 7298-7318.
- [2] J. P. Lange, E. van der Heide, J. van Buijtenen, R. Price, *ChemSusChem* **2012**, *5*, 150-166.
- [3] Y. Nakagawa, H. Nakazawa, H. Watanabe, K. Tomishige, *ChemCatChem* **2012**, *4*, 1791-1797.
- [4] H. Zhang, C. Canlas, A. Jeremy Kropf, J. W. Elam, J. A. Dumesic, C. L. Marshall, *J. Catal.* **2015**, *326*, 172-181.
- [5] A. Bohre, S. Dutta, B. Saha, M. M. Abu-Omar, *ACS Sustainable Chem. Eng.* **2015**, *3*, 1263-1277.
- [6] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411-2502.
- [7] M. J. Taylor, L. J. Dumdell, M. A. Isaacs, C. M. A. Parlett, K. Wilson, A. F. Lee, G. Kyriakou, *Appl. Catal., B* **2016**, *180*, 580-585.
- [8] S. G. Kulkarni, V. S. Bagalkote, S. S. Patil, U. P. Kumar, V. A. Kumar, *Propellants, Explos., Pyrotech.* **2009**, 520-525.
- [9] M. Audemar, C. Ciotonea, K. De Oliveira Vigier, S. Royer, A. Ungureanu, B. Dragoi, E. Dumitriu, F. Jerome, *ChemSusChem* **2015**, *8*, 1885-1891.
- [10] F. Dong, G. Ding, H. Zheng, X. Xiang, L. Chen, Y. Zhu, Y. Li, *Catal. Sci. Technol.* **2016**, *6*, 767-779.
- [11] C. P. Jiménez-Gómez, J. A. Cecilia, D. Durán-Martín, R. Moreno-Tost, J. Santamaría-González, J. Mérida-Robles, R. Mariscal, P. Maireles-Torres, *J. Catal.* **2016**, *336*, 107-115.
- [12] S. Srivastava, P. Mohanty, J. K. Parikh, A. K. Dalai, S. S. Amritphale, A. K. Khare, *Chin. J. Catal.* **2015**, *36*, 933-942.
- [13] D. Vargas-Hernández, J. M. Rubio-Caballero, J. Santamaría-González, R. Moreno-Tost, J. M. Mérida-Robles, M. A. Pérez-Cruz, A. Jiménez-López, R. Hernández-Huesca, P. Maireles-Torres, *J. Mol. Catal. A: Chem* **2014**, *383-384*, 106-113.
- [14] K. Yan, J. Liao, X. Wu, X. Xie, *RSC Advances* **2013**, *3*, 3853.
- [15] R. V. Sharma, U. Das, R. Sammynaiken, A. K. Dalai, *Appl. Catal., A* **2013**, *454*, 127-136.
- [16] B. M. Reddy, G. K. Reddy, K. N. Rao, A. Khan, I. Ganesh, *J. Mol. Catal. A: Chem* **2007**, *265*, 276-282.
- [17] B. M. Nagaraja, A. H. Padmasri, B. David Raju, K. S. Rama Rao, *J. Mol. Catal. A: Chem* **2007**, *265*, 90-97.
- [18] L. Liu, H. Lou, M. Chen, *Int. J. Hydrogen Energy* **2016**.
- [19] 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.* **2016**, *6*, 1754-1763.
- [20] O. F. Aldosari, S. Iqbal, P. J. Miedzian, G. L. Brett, D. R. Jones, X. Liu, J. K. Edwards, D. J. Morgan, D. K. Knight, G. J. Hutchings, *Catal. Sci. Technol.* **2016**, *6*, 234-242.
- [21] M. Li, Y. Hao, F. Cárdenas-Lizana, M. A. Keane, *Catal. Commun.* **2015**, *69*, 119-122.
- [22] K. Watanabe, *Molecules* **2013**, *18*, 3183-3194.
- [23] M. J. Campos Molina, R. Mariscal, M. Ojeda, M. Lopez Granados, *Bioresour. Technol.* **2012**, *126*, 321-327.
- [24] K. Watanabe, N. Yamagiwa, Y. Torisawa, *Org. Process Res. Dev.* **2007**, *11*, 251-258.
- [25] V. Antonucci, J. Coleman, J. B. Ferry, N. Johnson, M. Mathe, J. P. Scott, J. Xu, *Org. Process Res. Dev.* **2011**, *15*, 939-941.
- [26] C. Gozlan, R. Lafon, N. Duguet, A. Redl, M. Lemaire, *RSC Adv.* **2014**, *4*, 50653-50661.
- [27] A. Hfaiedh, K. Yuan, H. Ben Ammar, B. Ben Hassine, J. F. Soule, H. Doucet, *ChemSusChem* **2015**, *8*, 1794-1804.
- [28] S. Sakamoto, *Chim. Oggi* **2013**, *31*, 24-27.
- [29] C. Antonetti, E. Bonari, D. Licursi, O. D. N. N. Nassi, A. M. Raspollini Galletti, *Molecules* **2015**, *20*, 21232-21253.
- [30] Z. Wu, E. Borretto, J. Medlock, W. Bonrath, G. Cravotto, *ChemCatChem* **2014**, *6*, 2762-2783.
- [31] A. M. Raspollini Galletti, C. Antonetti, M. Bertoldo, F. Piccinelli, *Appl. Catal., A* **2013**, *468*, 95-101.
- [32] V. Hessel, G. Cravotto, P. Fitzpatrick, B. S. Patil, J. Lang, W. Bonrath, *Chem. Eng. Process.* **2013**, *71*, 19-30.
- [33] M. Irfan, M. Fuchs, T. N. Glasnov, C. O. Kappe, *Chemistry* **2009**, *15*, 11608-11618.
- [34] G. Vanier, *Synlett* **2007**, 131-135.
- [35] A. Y. Li, M. Kaushik, C.-J. Li, A. Moores, *ACS Sustainable Chem. Eng.* **2016**, *4*, 965-973.
- [36] K. Baranowska, J. Okal, W. Tylus, *Appl. Catal., A* **2016**, *511*, 117-130.
- [37] M. Blosi, S. Albonetti, S. Ortelli, A. L. Costa, L. Ortolani, M. Dondi, *New J. Chem.* **2014**, *38*, 1401-1409.
- [38] L. Delannoy, G. Thrimurthulu, P. S. Reddy, C. Methivier, J. Nelayah, B. M. Reddy, C. Ricolleau, C. Louis, *Phys. Chem. Chem. Phys.* **2014**, *16*, 26514-26527.
- [39] G. Águila, F. Gracia, J. Cortés, P. Araya, *Appl. Catal., B* **2008**, *77*, 325-338.
- [40] Z. Liu, M. D. Amiridis, Y. Chen, *J. Phys. Chem. B* **2005**, *109*, 1251-1255.
- [41] F. S. Delk, A. Våvere, *J. Catal.* **1984**, *85*, 380-388.
- [42] B. Wang, C. Wen, Y. Cui, X. Chen, Y. Dong, W.-L. Dai, *RSC Adv.* **2015**, *5*, 29040-29047.
- [43] Y. Lykhach, S. M. Kozlov, T. Skala, A. Tovt, V. Stetsovych, N. Tsud, F. Dvorak, V. Johaneck, A. Neitzel, J. Myslivecek, S. Fabris, V. Matolin, K. M. Neyman, J. Libuda, *Nat. Mater.* **2016**, *15*, 284-288.
- [44] C. T. Campbell, *Nat. Chem.* **2012**, *4*, 597-598.
- [45] S. Bagheri, N. Muhd Julkapli, S. Bee Abd Hamid, *Sci. World J.* **2014**, *2014*, 727496.

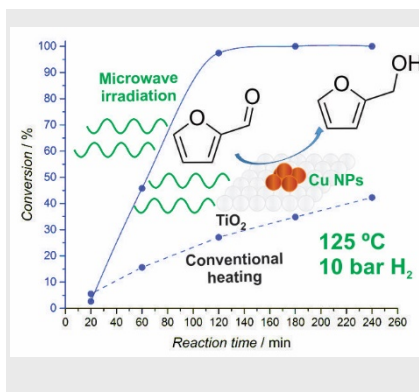
- [46] J. Lee, S. P. Burt, C. A. Carrero, A. C. Alba-Rubio, I. Ro, B. J. O'Neill, H. J. Kim, D. H. K. Jackson, T. F. Kuech, I. Hermans, J. A. Dumesic, G. W. Huber, *J. Catal.* **2015**, *330*, 19-27.
- [47] E. A. Anumol, P. Kundu, P. A. Deshpande, G. Madras, N. Ravishankar, *ACS Nano* **2011**, *5*, 8049-8061.
- [48] C. O. Kappe, B. Pieber, D. Dallinger, *Angew. Chem. Int. Ed. Engl.* **2013**, *52*, 1088-1094.
- [49] A. de la Hoz, A. Diaz-Ortiz, A. Moreno, *Chem. Soc. Rev.* **2005**, *34*, 164-178.
- [50] M. B. Gawande, S. N. Shelke, R. Zboril, R. S. Varma, *Acc. Chem. Res.* **2014**, *47*, 1338-1348.
- [51] X. Zhang, D. O. Hayward, D. Michael P. Mingos, *Chem. Commun.* **1999**, 975-976.
- [52] E. Heller, W. Lautenschläger, U. Holzgrabe, *Tetrahedron Lett.* **2005**, *46*, 1247-1249.

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Microwave-assisted Selective Hydrogenation of Furfural to Furfuryl Alcohol Employing a Green and Noble Metal-free Cu Catalyst