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# PAPER

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# Catalytic conversion of starch into valuable furan derivatives using supported metal nanoparticles on mesoporous aluminosilicate materials<sup>†</sup>

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Catalytically active supported metal nanoparticles on aluminosilicates including Cu and Pd-based systems were investigated in the microwave-assisted conversion to a range of valuable furanic compounds via tandem formic acid-promoted dehydration and subsequent selective hydrogenation processes. Results show that interesting selectivities to reduced products including 5-methylfurfural and 5-methylfurfuryl alcohol as well as hydroxymethylfurfural and furfural could be obtained in various proportions depending on the type of catalyst and the investigated reaction conditions. The investigation of reaction parameters including time of reaction, type of catalyst, quantity of catalyst and formic acid content indicated that reaction conditions can in principle be fine-tuned to maximise selectivity towards individual products

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# Introduction

Biomass is considered the only sustainable source of organic carbon currently available on earth and consequently the ideal substitute for petroleum in the production of fuels, chemicals and materials.<sup>1</sup> The high structural and chemical complexity of most bio-based feedstocks (from the simplest polysaccharides to more complex lignocellulosics and lignin) has a decisive effect on catalysts and process design.<sup>1,2</sup> Typical petroleum catalysts designed to resist high temperatures and hydrophobic environments might not be as effective and stable under biomass processing conditions. Scientists have therefore been prompted to come up with alternative and innovative methodologies to translate the knowledge of oil processing chemistries to biomass. However, this translation is not so trivial. In spite of few reports on the direct processing of biomass to valuable products,<sup>2-5</sup> most protocols and methodologies to date have been aimed to convert simpler fractions (e.g. platform molecules) derived from biomass into a range of valuable products.<sup>2,6,7</sup>

Platform molecules (aka building blocks) relate to chemical entities with multiple functionalities that can have a range of applications similar to petroleum-derived products in existing markets.<sup>8,9</sup> These include sugars and polyols (e.g. glucose,

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sorbitol, glycerol), organic acids (e.g. succinic, levulinic, itaconic, lactic acids) and furans (e.g. hydroxymethylfurfural - HMF and furfural).

Sugars and polysaccharides are interesting compounds which have been shown an interesting potential to be converted into furanics.3,4,10 Several reports have been recently aimed to maximise HMF and furfural yields from polysaccharides including starch11,12 and cellulose.13-17 Among these, recent work by Ranoux et al. pointed out that the conversion of hexoses (e.g. fructose) is an autocatalytic process by formic acid concomitantly formed with levulinic after a rehydratation process.18

We have recently developed an innovative one step approach to the conversion of simple sugars such as glucose into furan derivatives including HMF and reduced furan compounds (e.g. 5-methylfurfural or MF, 5-methylfurfuryl alcohol or MFA, dimethyl furan or DMF-, etc.) using a Cu-based aluminosilicate bifunctional catalytic system.<sup>19</sup> The protocol followed a microwave-assisted tandem formic acid-promoted dehydration of glucose to HMF and further selective hydrogenation to MFA, taking advantage of the decomposition of formic acid (FA) to  $H_2$  and  $CO + CO_2$  under the investigated conditions (Scheme 1).<sup>21,22</sup> Cu-containing nanomaterials were proved to be a cheaper and more environmentally friendly alternative as compared to more expensive noble metal systems.19

Based on these preliminary results with glucose, we have been prompted to explore the possibility to work with more complex feedstocks including polysaccharides (e.g. starch), aiming to future work towards waste-derived

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<sup>†</sup> In memoriam of Prof. Juan M. Campelo, inspiration for this work, who passed away in October 2012.

Paper



Scheme 1 Pathways and steps for the conversion of starch-derived materials into valuable furanics. Adapted from ref. 23. Reproduced by permission of the Royal Society of Chemistry.

feedstocks (*e.g.* biorefinery-derived syrups enriched in C5 oligomers and sugars).<sup>24</sup>

In this work, we aim to report our latest results on the conversion of starch to furanics using a range of mesoporous aluminosilicate supported nanoparticle Cu and Pd-systems under microwave irradiation. Several parameters have been studied including time of reaction, quantity of formic acid, quantity of catalyst as well as type of catalyst in our aim to a better understanding of the multistep processes taking place under the investigated conditions.

### Experimental

#### Materials syntheses

Parent Al-SBA-15 supports (with and without Zn) and from them Cu and Pd-based materials were synthesized following a previously reported procedure.<sup>19</sup> For the preparation of Cu materials, 1 g solid support and 0.057 g CuCl<sub>2</sub>·2H<sub>2</sub>O reagent grade purchased from Sigma-Aldrich (equivalent to a 2 wt.% Cu) were milled together in a planetary ball mill (Retsch 100) under previously reported optimised conditions (350 rpm, 10 min).<sup>19,25</sup> Upon incorporation of the metal, the sample was calcined at 400 °C (4 h, in air). Similarly, Pd-containing aluminosilicates (Pd/AlZn–SBA and Pd/Al–SBA) with a theoretical loading of 0.5 wt.% Pd were also synthesized using palladium acetate as metal precursor (Sigma-Aldrich, purity: 98%) following an identical ball-milling methodology.

#### Characterisation

Materials were characterized using nitrogen physisorption, EDX, X-Ray photoelectron spectroscopy (XPS), and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTs) as previously reported.<sup>19</sup>

Nitrogen adsorption measurements were carried out at 77 K using an ASAP 2000 volumetric adsorption analyzer from Micromeritics. The samples were outgassed for 24 h at 100 °C under vacuum ( $p < 10^{-2}$  Pa) and subsequently analysed. The linear part of the BET equation (relative pressure between 0.05 and 0.30) was used for the determination of the specific surface area. Mean pore size diameter ( $D_{BJH}$ ) and pore volumes ( $V_{BJH}$ ) were obtained from porosimetry data.

Elemental composition of the calcined samples was obtained using a JEOL JSM-6300 Scanning Microscope with energy-dispersive X-Ray analysis (EDX) at 20 kV. Samples were coated with Au/Pd on a high resolution sputtering SC7640 instrument at a sputtering rate of 1.5 kV per minute, up to 7 nm thickness.

The metal content in the materials was determined using Inductively Coupled Plasma (ICP) in a Philips PU 70000 sequential spectrometer equipped with an Echelle monochromator (0.0075 nm resolution) and couple to Mass Spectrometry. Samples were digested in HNO<sub>3</sub> and subsequently analysed by ICP at the SCAI of Universidad de Cordoba.

#### Catalytic experiments

Microwave experiments were carried out in a CEM-DISCOVER model with PC control. Experiments were performed on a closed vessel (pressure controlled) under continuous stirring. The microwave method was generally power-controlled where reactions mixture were irradiated with the maximum power output (300 W), achieving different temperatures in the 167–186 °C range (average temperature 178 °C), as measured by an infra-red probe. Pressures developed in the system ranged from 213 to 250 psi (15–17 bar), with an average of 245 psi (17 bar).<sup>19</sup>

In a typical reaction, 50 mg starch from potato purchased from Sigma-Aldrich were suspended in 0.5 mL water, then 0.5 mL formic acid (Sigma-Aldrich, purity > 96%) was added with 0.02 g catalyst and microwaved at 300 W for a short period of time (typically between 5–30 min). Upon cooling, the reaction mixture was filtered off and subsequently analyzed (to confirm the presence of the furanic-like compounds) by GC/GC–MS using an Agilent 6890 N GC model fitted with a HP-5 capillary column and an FID detector.

Quantitative reaction runs were analysed in a HPLC Model Series 200 (Perkin Elmer) provided with a Refractive Index Detector (L-2490) and an Ascentis Express  $C_{18}$  column (10 cm × 4.6 mm, 2.7  $\mu$ m), operating with a mobile phase of 5% acetonitrile/95% water at a flow of 1.2 mL min<sup>-1</sup> at the SCAI of Universidad de Cordoba (Spain).

Reused experiments were carried out by triplicating reagent and catalyst quantities (to ensure enough catalyst was present for each reuse) under otherwise identical conditions to those stated in typical reaction runs. Upon reaction completion, catalysts were filtered off, washed thoroughly with ethanol and acetone and dried at 120 °C prior to their next use with fresh reagents.

# Results and discussion

Supported nanoparticles Cu and Pd-systems on mesoporous SBA-15 materials were previously characterised by XRD, N<sub>2</sub>

physisorption, XPS and DRIFTS.<sup>19</sup> A summary of the textural properties of synthesized materials is included in Table 1.

The incorporation of Cu or Pd did not have a significant influence in terms of textural and structural properties with respect to their parent aluminosilicates, but generally textural properties including surface areas and pore volumes decreased upon ball-mill metal incorporation (Table 1). Total acidity of the materials was generally moderate to low as well as their Lewis acidities as compared with commercial zeolites and analogous materials (*ca.* 250–350 µmol g<sup>-1</sup>), insufficient to promote hydrolysis or dehydration reactions in the absence of formic acid. Formic acid was purposely added as useful hydrogen donating solvent and co-catalyst (to promote hydrolysis/dehydration reactions) in the selected chemistries.

An interesting more "metallic" character for nanoparticles (both Pd and Cu) probably via metal-Zn interaction was observed in the conversion of glucose even at the very low quantities of Zn present in the materials as was observed and investigated in detail in a recent report of the group.<sup>19</sup> The role of Zn was claimed to be related to substrate activation (via binding to OH groups of glucose) inducing hydrogenolytic reactivity with metal-H species in the materials as recently suggested by Parsell et al. in hydrogeoxygenation of lignin model compounds.<sup>26</sup> The incorporation of palladium onto the support did not significantly affect the acidity of the synthesized materials. However, a slight increase in Lewis acidity could be observed for Cu containing materials as expected. Regarding the acidity of the aluminosilicate material used as support, it can be observed that the mesoporous support containing Zn possessed lower Brönsted acidity which can be explained by the fact of a significant decrease in Al content as compared to Al-SBA-15 support (see Table 1) which in turn decreased its Brönsted acidity.

The main activities of the catalysts in the microwaveassisted aqueous conversion of starch have been summarised in Table 2 and Fig. 1–4.

Blank runs provided moderate activities (<50%) only at long times of microwave irradiation (>60 min). Low conversions were observed in the systems at shorter times of reaction under microwave irradiation. Comparative reactions under conventional heating did not yield any appreciable quantities to products (conversion <30%) even after 2 h reaction. Formic acid (FA) was the reason of the moderate

Table 1 Textural properties of mesoporous materials synthesized in this wor	Table 1	Textural properties of	mesoporous materials	synthesized in this wo	rk <sup>a</sup>
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Surface area $(m^2 g^{-1})$	Pore size (nm)	Pore volume $(mL g^{-1})$	Al content (%)	Brönsted acidity $(\mu mol \ g^{-1})$	Lewis acidity $(\mu mol g^{-1})$				
647	7.0	0.82	1.3	88	45				
912	9.2	1.25	0.22	35	37				
509	6.8	0.77	1.1	60	97				
662	8.9	0.98	0.2	59	70				
507	8.5	0.92	b	46	52				
642	9.0	0.94	b	34	36				
	Surface area (m <sup>2</sup> g <sup>-1</sup> ) 647 912 509 662 507 642	Surface area (m <sup>2</sup> g <sup>-1</sup> ) Pore size (nm)   647 7.0   912 9.2   509 6.8   662 8.9   507 8.5   642 9.0	Surface area $(m^2 g^{-1})$ Pore size $(nm)$ Pore volume $(mL g^{-1})$ $647$ 7.0 $0.82$ $912$ $9.2$ $1.25$ $509$ $6.8$ $0.77$ $662$ $8.9$ $0.98$ $507$ $8.5$ $0.92$ $642$ $9.0$ $0.94$	Surface area $(m^2 g^{-1})$ Pore size $(nm)$ Pore volume $(mL g^{-1})$ Al content $(\%)$ 6477.00.821.39129.21.250.225096.80.771.16628.90.980.25078.50.92 $-^b$ 6429.00.94 $-^b$	Surface area ( $m^2 g^{-1}$ )Pore size ( $nm$ )Pore volume ( $mL g^{-1}$ )Al content ( $\%$ )Brönsted acidity ( $\mu mol g^{-1}$ )6477.00.821.3889129.21.250.22355096.80.771.1606628.90.980.2595078.50.92 $-^b$ 466429.00.94 $-^b$ 34				

<sup>*a*</sup> Average mesopore diameters were estimated from the adsorption branch of the nitrogen isotherm using the BJH method. BET surface area was estimated by multipoint BET method using the adsorption data. Mesopore volume from the isotherms at relative pressure of 0.95. <sup>*b*</sup> Not measured.

Table 2 Catalytic activity of investigated materials in the conversion of starch to furanics<sup>a</sup>

Catalyst	Conversion (mol%)	Sel. HMF (mol%)	Sel. furf. (mol%)	Sel. reduced products <sup>c</sup> (mol%)	Sel. others <sup>d</sup> (mol%)
Blank (no cat.) <sup>b</sup>	<50	<10	15	55 (mixture)	30
Al–SBA (no FA)	$<\!\!20$	_	_		_
Al-SBA	>95	_	21	55 (mixture)	$<\!\!25$
AlZn-SBA	>95	_	13	62 (mixture)	$<\!\!25$
1.5% Cu/Al-SBA	>99	_	10	$> 80^{e}$	< 10
2% Cu/AlZn-SBA	>99	_	15	75 <sup>e</sup>	10
0.5% Pd/Al–SBA	>95	_	10	>85 (mixture)	<5
0.5% Pd/AlZn-SBA	>99	—	<5	>85 (mixture)	< 10

<sup>*a*</sup> Reaction conditions: 0.05 g starch, 0.5 mL H<sub>2</sub>O, 0.5 mL formic acid, 0.02 g catalyst, microwaves, 300 W (maximum temperature reached 183 °C, average temperature 182 °C), 30 min reaction. <sup>*b*</sup> Reaction after 60 min reaction. <sup>*c*</sup> MF and MFA (major products) as well as traces of DMF, MTHFA, AL and LA were detected as reduced products observed under the investigated conditions. <sup>*d*</sup> Selectivity to others mostly account for humins and polycondensed products generated in the reaction. <sup>*e*</sup> MFA (selectivity > 60%) was the major product obtained in catalysed reactions by Cu and Pd-containing systems.



Fig. 1 Selectivity changes to HMF (Y axis, mol%) at different times of reaction for AlZn–SBA catalytic systems in the microwave-assisted conversion of starch. Reaction conditions: 0.05 g starch, 0.5 mL H<sub>2</sub>O, 0.5 mL formic acid, 0.02 g catalyst, microwaves, 300 W (maximum temperature reached 183 °C, average temperature 180 °C), varying reaction times from 2 to 30 min.



Fig. 2 Selectivity changes to reduced products (Y axis, mol%) at different times of reaction for AlZn-SBA catalytic systems in the microwave-assisted conversion of starch. Reaction conditions: 0.05 g starch, 0.5 mL H<sub>2</sub>O, 0.5 mL formic acid, 0.02 g catalyst, microwaves, 300 W (maximum temperature reached 183 °C, average temperature 180 °C), varying reaction times from 2 to 30 min.

conversion in the systems as playing the role of starch hydrolysis and subsequent dehydration co-catalyst apart from its



Fig. 3 Differential product selectivity (X axis, mol%) for Cu and Pd/AlZn–SBA catalytic systems in the microwave-assisted conversion of starch. Reaction conditions: 0.05 g starch, 0.5 mL H<sub>2</sub>O, 0.5 mL formic acid, 0.02 g catalyst, microwaves, 300 W (maximum temperature reached 183 °C, average temperature 180 °C), 30 min reaction.



Fig. 4 Changes in selectivity (Y axis, mol%) for the production of HMF (white bars) vs. reduced products (red. prod., black bars) of various metal/AlZn-SBA catalytic systems in the microwave-assisted conversion of starch. Reaction conditions: 0.05 g starch, 0.5 mL H<sub>2</sub>O, 0.5 mL formic acid, 0.02 g catalyst, microwaves, 300 W (maximum temperature reached 183 °C, average temperature 181 °C), 5 min reaction time.

role as hydrogen-donating reagent (*via* decomposition into hydrogen and  $CO + CO_2$ ).<sup>21,22</sup> The acidity of FA was reported to be sufficient to promote acidolytic cleavage of lignin bonds<sup>21,22</sup> and in fact reactions in the absence of FA provided

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low conversions to products (Table 2, Al–SBA no FA entry). The relatively low acidity of the aluminosilicate systems was not sufficient to trigger the initial dehydration step to a large extent. Interestingly, analogous reactions conducted in isopropanol/NaOH systems gave rise to a significant generation of humins and polycondensed products (>90%) under otherwise identical conditions to those of FA-catalysed processes.

In terms of product formation, reduced species from HMF such as MF and MFA and MTHFA were observed to be present in blank runs even if in small quantities (Table 2). HMF was only found to be obtained at short times of reaction.

A multistep reaction takes place in starch conversion, commencing with hydrolysis of the polysaccharide to glucose units followed by isomerisation of glucose to fructose and subsequent dehydration of the monosaccharide to HMF. Interestingly, levulinic acid (LA) was not observed to be formed from HMF in any blank runs even in the presence of increased quantities of formic acid. A range of by-products are generally formed in the process, derived from condensation reactions of intermediates and/or HMF (*e.g.* humins > 20%).<sup>4,27–29</sup> Furfural was also observed in all experiments reported in this work which is believed to be produced from C–C cleavage of 2 condensed HMF molecules at the 5-position (Scheme 1).

Compared to blank runs, the use of aluminosilicates provided an additional increase in activity, reaching conversions in the range of 85–90% only after 5–10 minutes of reaction under microwave irradiation. Microwave-assisted reactions provided relatively high selectivities to a mixture of reduced products including MF and MFA, being that slightly superior for AlZn–SBA which supports previous claims on the effect of Zn in the systems.<sup>19</sup> The activities of metal-containing systems were generally similar to those of the parent aluminosilicates but selectivities to reduced products were improved, being remarkably more selective to the production of MFA (Table 2, Fig. 2). FA decomposition (into hydrogen and CO + CO<sub>2</sub>) was essential for the selective hydrogenolysis/hydrogenation of HMF to MF and particularly MFA (Scheme 1), which was favoured on the *in situ*-reduced metal sites.

Several parameters were investigated in the microwaveassisted methodology, namely the quantity of catalyst and formic acid and the time of reaction (Fig. 1) to further see trends in the production of furanics in the systems. Results are depicted in Fig. 1-4 for the case of the most relevant supported aluminosilicate materials for each one of the major target compounds. Initially, an investigation on the quantity of catalysts in the reactions (results not shown) indicated significantly reduced activities for quantities of catalysts under 0.02 g, while larger quantities (>0.02 g) did not provide any particular improvements on conversions or selectivities. Therefore, 0.02 g catalyst was selected as optimum for subsequent experiments. With regards to the quantity of formic acid, larger quantities to 0.5 mL in the systems provided an increasing number of products, particularly polycondensed humin-like compounds. Comparatively, reactions run with half FA content (0.25 mL) gave lower conversion in the systems (due to the catalytic effect of FA in the first step of starch hydrolysis). Therefore 0.5 mL FA was selected as optimum content for the reaction.

Fig. 1 depicts changes in HMF production at different times of reaction. Of note are the almost quantitative conversions in all systems (including aluminosilicate supports) after 5 min of reaction. Results from Table 2 indicated that HMF was not observed after 30 min reaction in any of the studied supported nanoparticle systems (Table 2). Nevertheless, HMF could be obtained in reasonably high selectivities (up to 55–60 mol%) at high starch conversion (>85%) at very short times of reaction. At increasing times of reaction, the produced HMF was further hydrogenated to MF and MFA as well as underwent intermolecular condensation and then cleaved to furfural.

This was a general trend observed not only for increasing times of reaction (from 2 to 30 min) but also interestingly observed from the support to Cu and Pd-materials. Results were in good agreement with hydrogenation/hydrogenolytic activity of the systems which is expected to be maximised in Pd/Al(Zn)–SBA materials as compared to the Cu counterpart or the parent aluminosilicate (Fig. 1). The decrease in HMF production was accompanied by a concomitant increase in the generation of reduced furanics, namely MF and MFA as depicted in Fig. 2.

Interesting trends were also found between materials and times of reaction. The particular case of Pd/AlZn–SBA has been illustrated in Fig. 3, in which MFA was preferentially formed from a 2 step hydrogenation/dehydration (from HMF to MF) and subsequent hydrogenation of MF to MFA (Fig. 3).

The interesting Zn effect in the enhanced reducibility of furanic products is also clearly visible in Fig. 4 for both Pd- and Cu-based catalysts (see also reusability studies). Comparing both metal/Al–SBA and metal/AlZn–SBA materials, both Cu and Pd/AlZn–SBA were able to provide improved selectivities to reduced products as opposed to HMF (Fig. 4), even at short times of reaction (5 min).

The effect was also plausible at longer times of microwave irradiation in which advanced hydrogenated products (MFA, MTHFA) were obtained (see Fig. 3), in good agreement with previous reports.<sup>19,23</sup> Interestingly, Cu-based catalysts were efficient in the selective production of HMF, for which a maximum selectivity of *ca.* 70 mol% could be achieved after 5 min microwave irradiation using Cu/Al–SBA. These were slightly improved, but similar in any case, to those obtained in the conversion of glucose under analogous conditions.<sup>19</sup>

Comparably, Pd materials were confirmed to have a significantly larger hydrogenation activity in the production of hydrogenated products from HMF even at short times of reaction (Fig. 4). Interestingly, only trace quantities of AL, methyltetrahydrofurfurylalcohol (MTHFA) and formic acid 5-methyltetrahydrofurfuryl ester (from the coupling of MTHFA and formic acid) were observed in the course of our studies with starch. Some of these products were however found in relatively relevant quantities in glucose conversion under identical conditions. Starch produces a generally cleaner reaction profile which could possibly be related to the additional steps required (*e.g.* starch hydrolysis) to achieve smaller saccharide units to be further converted in the multistep process.

In any case, several relevant points can be drawn from the results. Firstly, Cu-containing materials were more selective and similarly active in the reaction under the investigated conditions but Pd materials show an interesting potential for further chemistries (*e.g.* hydrogenation to furancis as well as potential oxidation to maleic acid and furandicarboxylic acid). Secondly, a switchable product protocol is possible by simply selecting carefully the reaction conditions to focus on particular products (*e.g.* HMF, MF or MFA). Thirdly, and not less importantly, the supported nanoparticle systems are highly stable and reusable under the investigated reaction conditions as shown in Fig. 5 and 6.

The activities were only observed to slightly drop after 5 uses but no significant leaching of the copper or palladium phases was observed (<5 ppm as followed by ICP-MS), in good agreement with similar chemistries recently conducted in the group with Cu and Pd-based catalysts.<sup>30</sup> The minimum leaching observed is believed to be related to the high solubility of Cu species in acid media.<sup>31,32</sup> Results depicted in Fig. 5 for Cu/Al–SBA (similar to those of Cu/AlZn–SBA or Pd catalysts) proved that the catalysts were fully reusable under the studied conditions, preserving almost intact their initial activity after 5 uses. Similar values (not shown) were achieved for Pd-based catalysts.

Subsequently reuses of the catalyst exhibited almost identical selectivities to reduced products (>80%) but slightly improved selectivities to MFA cycle after cycle, with a decreased generation of by-products in the systems. This was a common trend for both AlZn–SBA and Al–SBA systems although the trend was more noticeable in Zn-containing materials. With the observed activity and leaching under the investigated reaction conditions, changes in activity could be due to the activity of stable Cu species in different environments which remained in the Cu catalyst after subsequent uses. Further investigations currently ongoing in our lab have



Fig. 5 Reuses of Cu/Al-SBA in the microwave-assisted conversion of starch to valuable products. Reaction conditions (each reuse): 0.15 g starch, 1.5 mL H<sub>2</sub>O, 1.5 mL formic acid, 0.06 g catalyst, 30 min, mw irradiation, 300 W, maximum temperature reached 180 °C (average temperature 179 °C).



Fig. 6 Conversion virtually unchanged after reuses of Cu/Al–SBA. Reaction conditions (each reuse): 0.15 g starch, 1.5 mL H<sub>2</sub>O, 1.5 mL formic acid, 0.06 g catalyst, 30 min, mw irradiation, 300 W, maximum temperature reached 180 °C (average temperature 179 °C).

been aimed to ascertain these rather unexpected selectivity changes in the reused catalysts.

## Conclusions

Supported metal nanoparticles on porous aluminosilicates have been proved to be highly active and differently selective to a range of furanics in the microwave-assisted conversion of starch using formic acid as dehydration co-catalyst and hydrogen-donating solvent. Catalysts were able to provide quantitative conversion of starting material after ca. 5-10 min reaction, with interesting selectivities (up to 70%) to HMF or alternatively reduced products, mostly MF and MFA. The potential of the protocol lies in the possibility to switch product generation (from HMF at short times of reaction to MF or MFA at varying conditions), representing an unprecedented protocol that may pave the way to future studies on related tandem chemistries (e.g. dehydration/oxidation; dehydration/esterification as well as C-C and C-O couplings). The proposed relevant chemistries can in principle be further translated into more scalable and condition-controllable flow processes which are envisaged to provide improved selectivities and process intensification in aqueous transformations of renewable resources that will be reported in due course.

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