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COMMUNICATION

Tunable copper-catalyzed chemoselective hydrogenolysis of biomass-derived γ -valerolactone into 1,4-pentanediol or 2-methyltetrahydrofuran†

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Direct conversion of γ -valerolactone, which is one of the most significant cellulose-derived compounds, into 1,4-pentanediol was carried out by chemoselective hydrogenolysis catalyzed by a simple yet versatile copper–zirconia catalyst. Depending on the reaction conditions, 2-methyltetrahydrofuran could also be obtained in excellent yields.

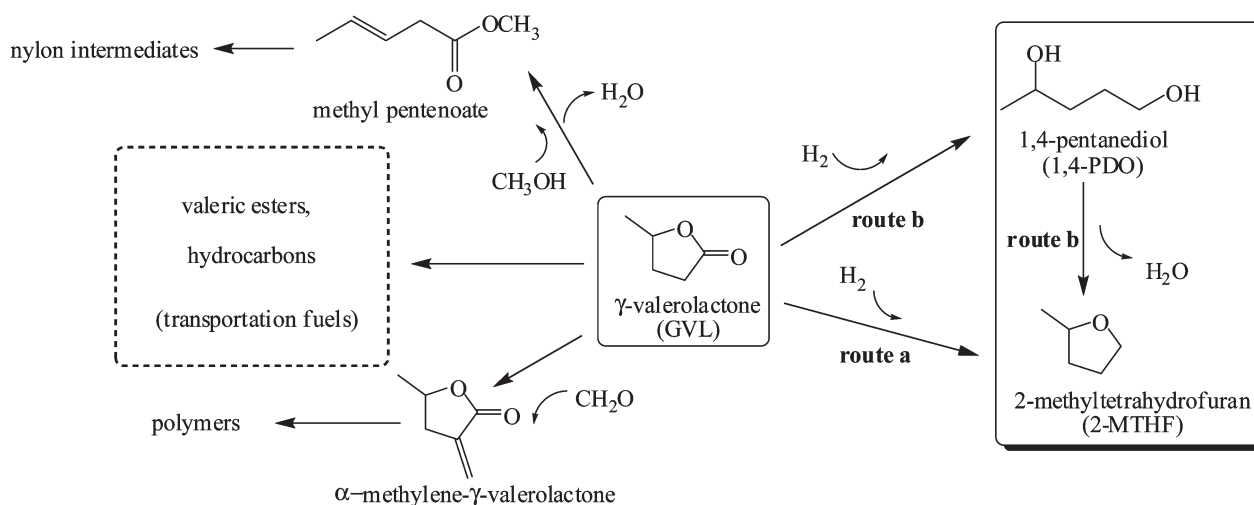
Utilization of renewable biomass for the chemical industry is becoming even more important in light of ever decreasing fossil resources and increased emission of greenhouse gases.¹ To prevent competition with food production, as seen in the last few years, non-food biomass should be used as a biomass resource for the manufacture of useful chemicals.² From a chemical point of view, biomass-derived raw materials contain excess functionality for use as fuels and chemicals, thus the challenge in this field is to develop efficient and practical methods to control the functionality in the final product.³ Accordingly, one effective strategy for the conversion of biomass is to first partially remove oxygen to produce a handful of well-identified reactive

intermediates, also known as bio-based platform molecules, followed by conversion of these compounds into desired products.⁴ In this respect, γ -valerolactone (GVL), accessible from abundant and inexpensive lignocellulosic biomass,⁵ has recently emerged as one of the most promising sustainable intermediates that can provide access to a variety of valuable chemicals.^{1b,6} As outlined in Scheme 1, a wide range of bio-based fuels, commodities and fine chemicals can subsequently be generated from GVL.

In contrast to tremendous efforts focused on the conversion of bio-derived GVL into renewable transportation fuels,⁷ there are scarcely any available reports dealing with the potential utilization of GVL for production of highly valuable 1,4-pentanediol (1,4-PDO) or 2-methyltetrahydrofuran (2-MTHF) (Scheme 1).⁸ Biogenic diols can be used as monomers to produce high performance biodegradable polyesters. Moreover, they are also important fine chemical intermediates applied in various fields.⁹ 2-MTHF is advocated as an alternative solvent in the pharmaceutical industry and also considered a part of P-series fuel.^{3,10} In this context, a simple multitask catalytic system that can readily allow flexible and selective conversion of GVL into either 1,4-PDO or 2-MTHF is highly desirable. However, the inherent chemical stability of GVL makes the controlled transformation of this molecule under mild conditions extremely difficult.^{8,11} Recently, Geilen *et al.*^{8b} have shown that a Ru-based molecular catalyst system bearing expensive phosphine

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Scheme 1 Reaction pathways for the production of value-added chemicals and fuels from biomass-derived GVL.

ligands in combination with ionic and/or acidic additives can selectively convert bio-derived levulinic acid (LA) into 1,4-PDO or 2-MTHF *via* intermediate formation of GVL. Despite its usefulness, clear drawbacks of this system include the inherent problems of non-reusability, necessity of special handling of metal complexes, high cost of catalyst preparation, as well as tedious work-up procedures.

During the search for a readily available, applicable, highly active and reusable catalyst for lignocellulosic biomass transformation,¹² we found that a simple non-noble-metal-based catalyst system comprising copper dispersed in a zirconia matrix can efficiently catalyze the controlled and selective hydrogenolysis of GVL. Copper-containing catalysts have been extensively employed in past decades for the selective elimination of NO_x,¹³ water-gas-shift reactions,¹⁴ synthesis and steam-reforming of methanol.¹⁵ Moreover, it is also established that copper catalysts are very selective for a number of hydrogenation or hydrogenolysis reactions, such as conversion of furfural to furfuryl alcohol,¹⁶ methyl ester to methyl alcohol,¹⁷ or the transformation of glycerol to the corresponding diols.¹⁸ Herein, we report the first versatile and tunable synthesis of 1,4-PDO or 2-MTHF from the chemoselective hydrogenolysis of GVL by means of a heterogeneous Cu/ZrO₂ catalyst system. To the best of our knowledge, this flexible Cu-mediated catalysis represents the most efficient, simple, and eco-friendly catalytic system for the convenient and controlled synthesis of higher value-added chemicals from biomass-derived GVL to date.

Initially, a series of copper–zirconia catalysts (denoted as Cu/ZrO₂-OG, see the ESI† for experimental details), prepared by an oxalate-gel-coprecipitation method previously developed by our group,¹⁵ were applied for the hydrogenolysis of GVL in ethanol under 6 MPa H₂ at 200 °C. Prior to the reaction, the Cu/ZrO₂-OG catalyst was activated under 5 vol% H₂-Ar at 300 °C for 2 h. Table 1 demonstrates that selective production of 1,4-PDO in a 37% yield could be achieved when 10 wt% Cu/ZrO₂-OG is used (Table 1, entry 1). An increase in Cu loading to 20 wt% significantly increased the 1,4-PDO yield to 67% (Table 1, entry 2). The highest product yield is 96% when Cu loading was increased to 30 wt% (Table 1, entry 3). However, a further increase in the Cu loading to 40 wt% led to a slight decrease in the desired product yield (Table 1, entry 4). We also investigated the repeated uses of the 30 wt% Cu/ZrO₂-OG catalyst for GVL conversion. Much to our delight, GVL conversion and 1,4-PDO yield decreased only slightly after three repeated uses (Table 1, entry 5); inductively coupled plasma (ICP) analysis showed that no Cu was present in the filtrate, indicating its high stability and reusability. This result is remarkable, and becomes more relevant as the reaction can also proceed smoothly in *n*-butanol with the 30 wt% Cu/ZrO₂-OG catalyst, although a longer reaction time is required (Table 1, entry 6). This high activity for conversion of GVL in *n*-butanol has practical implications, because we have shown elsewhere that GVL can be obtained from deconstruction of cellulose through *n*-butanol-mediated reactive extraction protocol.^{12b}

The present Cu (10–40 wt%)/ZrO₂-OG catalysts were characterized to clarify the origin of their high GVL hydrogenolysis activities. Typical data such as metal loadings, Brunauer–Emmet–Teller (BET) surface areas and Cu metal surface areas (determined from chemical N₂O titration) are summarized in

Table 1 Hydrogenolysis of GVL into 1,4-PDO with various catalysts^a

Entry	Catalyst	Metal loading (wt%)	Conv. ^h (%)	Selectivity ^h (%)	
				1,4-PDO	2-MTHF
1	Cu/ZrO ₂ -OG	10	38	97	3
2	Cu/ZrO ₂ -OG	20	68	98	2
3	Cu/ZrO ₂ -OG	30	97	99	1
4	Cu/ZrO ₂ -OG	40	92	99	1
5 ^b	Cu/ZrO ₂ -OG	30	95	98	2
6 ^c	Cu/ZrO ₂ -OG	30	92	99	1
7 ^d	Cu/ZrO ₂ -CP	30	41	98	2
8 ^e	Cu/ZrO ₂ -IMP	30	10	98	2
9	Cu/ZnO-OG	30	52	99	1
10	Cu/Al ₂ O ₃ -OG	30	71	90	10
11	Cu/MgO-OG	30	n.r.	—	—
12 ^f	ZrO ₂	0	n.r.	—	—
13 ^g	Cu powder	100	n.r.	—	—
14	Ru/C	5	2	n.d.	n.d.
15	Ru/ZrO ₂	5	3	n.d.	n.d.
16	Ru/ZnO	5	1	n.d.	n.d.
17	Ru/Al ₂ O ₃	5	2	n.d.	n.d.

^a Reaction conditions: GVL (5 mmol), ethanol (10 mL), catalyst (0.1 g), H₂ pressure (6 MPa), T (200 °C), t (6 h); all oxide precursors were prepared by calcination in air at 600 °C for 4 h; n.r. = no reaction; n.d. = non-detectable. ^b Reused three times. ^c *n*-Butanol (10 mL) was used instead of ethanol, t (10 h). ^d Cu/ZrO₂-CP prepared by co-precipitation with Na₂CO₃. ^e Cu/ZrO₂-IMP prepared by impregnation. ^f ZrO₂ prepared by oxalate-gel coprecipitation followed by calcination in air at 600 °C. ^g Cu powder purchased from Alfa Aesar. ^h Conversion and selectivity determined by GC and GC-MS.

Table S1 of ESI.† It is seen that there is only a weak relationship between the BET surface area or particle sizes and the performance of the Cu/ZrO₂-OG samples, indicating that the external texture is not the key factor governing the catalytic performance of the present samples prepared by oxalate-gel-coprecipitation. However, by a careful correlation of the metallic Cu surface area data included in Table S1,† it could be found that there is a good relationship between the metallic copper surface areas and the performance of the Cu/ZrO₂-OG catalysts with various Cu loadings. Therefore, the fact that the specific composition of 30 wt% Cu/ZrO₂-OG sample can substantially maximize the exposure of the fraction of catalytically active species at the catalyst surface is crucial for achieving high activity in the GVL hydrogenation, in line with the broad literature documenting the structure–activity relationship for supported copper catalysts.¹⁵

As for the 30 wt% Cu/ZrO₂-OG sample, X-ray diffraction (XRD) patterns of the calcined form of the as-synthesized catalyst showed merely tetragonal ZrO₂ and CuO crystallites (Fig. 1). After pre-reduction under 5 vol% H₂-Ar atmosphere at 300 °C for 2 h, a strong peak positioned at 43.3° ascribed to (111) lattice plane of the metal Cu appeared. This, together with the fact that no diffraction features of CuO could be identified in the reduced form of the catalyst, indicates that CuO was completely reduced into metallic Cu in the working sample. The average size of the resultant Cu⁰ particles was estimated to be *ca.* 15 nm based on Scherrer equation analyses.¹⁵ This scenario could be further corroborated by the temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS) analysis (see Fig. S1–S3, ESI†). The high stability and reusability of the 30 wt% Cu/ZrO₂-OG catalyst in the hydrogenolysis

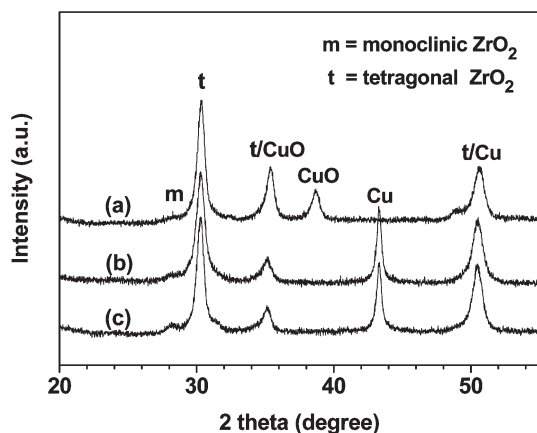


Fig. 1 XRD patterns of 30 wt% Cu/ZrO₂-OG: (a) calcined at 600 °C for 4 h; (b) reduced form of (a) at 300 °C in 5% H₂-Ar for 2 h; (c) after three repeated runs under reaction conditions in Table 1, entry 5.

reaction are compatible to the XRD and XPS results. Indeed, XRD and XPS results show no obvious changes in the mean diameters of the Cu nanoparticles and in the metallic state of Cu, respectively, after three successive runs (Fig. 1 and Fig. S3, ESI†).

In a comparison of other Cu/ZrO₂ catalysts with identical Cu loadings prepared by conventional co-precipitation and impregnation methods (Table 1, entries 7 and 8), it is observed that the Cu/ZrO₂-OG featuring higher component dispersion is more effective (see Table S1, ESI†), as demonstrated by the higher activities observed for the oxalate gel-derived catalyst. As the choice of the support plays an important role in metal catalysis, we also evaluate copper supported on ZnO, Al₂O₃ and MgO (Cu/ZnO-OG, Cu/Al₂O₃-OG and Cu/MgO-OG) prepared by the oxalate gel-coprecipitation method. The use of ZnO and Al₂O₃ as supports resulted in the formation of the desired product 1,4-PDO in moderate yields (Table 1, entries 9 and 10), but the Cu/MgO-OG catalyst was almost inactive in the study reaction (Table 1, entry 11). On the other hand, 1,4-PDO was not observed with pure ZrO₂ (Table 1, entry 12), which strongly confirmed that the presence of dispersed copper was essential for the high activity observed in the hydrogenolysis of GVL. In addition, the reaction hardly proceeds when bulk Cu powder (average size *ca.* 150 nm) was used (Table 1, entry 13). Since heterogeneous ruthenium-based catalysts have received much attention for the selective hydrogenation or hydrogenolysis of a wide variety of carboxylic acids and esters,¹⁹ we also evaluated several Ru-based materials including Ru/C, Ru/ZrO₂, Ru/ZnO and Ru/Al₂O₃ as catalysts in GVL hydrolysis. However, the yield toward the desired 1,4-PDO product was found to be less than 3% under identical reaction conditions (Table 1, entries 14–17).

Having established that Cu/ZrO₂-OG is able to chemoselectively catalyze hydrogenolysis of GVL into 1,4-PDO, our attention shifted toward the conversion of GVL into 2-MTHF using the same catalyst system. With the 30 wt% Cu/ZrO₂-OG catalyst, we first studied the effect of hydrogen pressure on the hydrogenolysis of GVL at 200 °C (Fig. 2). The reaction rate increased smoothly as the hydrogen pressure was raised from 2 to 4 MPa,

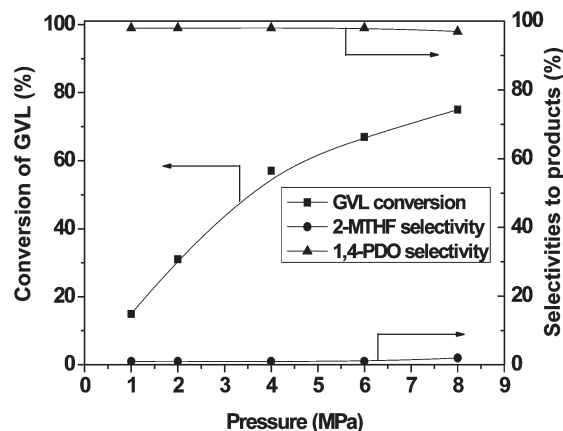


Fig. 2 The pressure-dependent performance of the 30 wt% Cu/ZrO₂-OG catalyst for GVL hydrogenolysis. Reaction conditions: GVL (5 mmol), ethanol (10 mL), catalyst (0.1 g), T (200 °C), t (2 h).

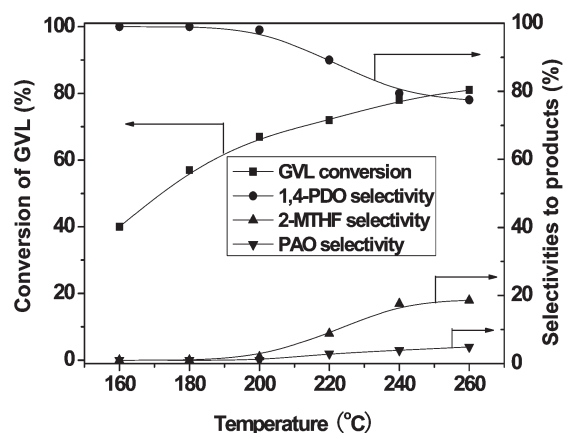


Fig. 3 The temperature-dependent performance of the 30 wt% Cu/ZrO₂-OG catalyst for GVL hydrogenolysis. Reaction conditions: GVL (5 mmol), ethanol (10 mL), catalyst (0.1 g), H₂ pressure (6 MPa), t (2 h).

but increased slowly at 4–8 MPa. The major product was 1,4-PDO under all the reaction conditions examined. Meanwhile, studies on the effect of the reaction temperature at 6 MPa hydrogen pressure revealed that the reaction also proceeded at lower temperature, but again no desirable formation of 2-MTHF could be achieved (Fig. 3). The most significant finding, however, was that appreciable amounts of 2-MTHF (*ca.* 6%) were produced as the main by-product when the reaction was performed at a slightly higher temperature of 220 °C. Of yet further interest was that increasing the reaction temperature to 240 °C led to an obvious increase in the yield of the 2-MTHF (*ca.* 13%). Nevertheless, the 2-MTHF yield remained constant with further increasing the reaction temperature up to 260 °C.

In an attempt to improve the yield toward 2-MTHF synthesis, subsequent studies were focused on the hydrogenolysis of GVL at 240 °C over a series of 30 wt% Cu/ZrO₂-OG with significantly modified acidic properties of the catalyst surface obtained by calcination in air at different temperatures in the range of 300–700 °C for 4 h (see Fig. S4 and S5, ESI†), whereby we

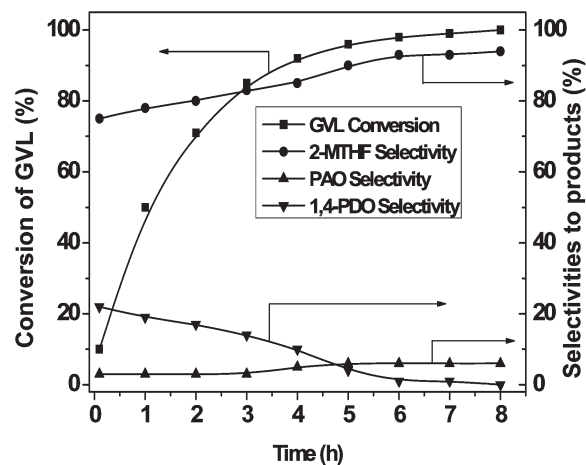
Table 2 Tunable selective hydrogenolysis of GVL into 2-MTHF or 1,4-PDO with various 30 wt% Cu/ZrO₂-OG catalysts^a

Entry	Calcination temperature (°C)	Conv. ^b (%)	Selectivity ^b (%)		
			2-MTHF	1,4-PDO	PAO
1	300	94	93	0	7
2	400	98	93	1	6
3	500	98	66	30	4
4	600	96	21	76	3
5	700	78	11	86	3

^a Reaction conditions: GVL (5 mmol), ethanol (10 mL), catalyst (0.1 g), H₂ pressure (6 MPa), T (240 °C), t (6 h). ^b Conversion and selectivity determined by GC and GC-MS.

took into account previous findings by Geilen *et al.*^{8b} that the control of the dehydration reactions by a careful modulation of the acidity of the reaction medium is important for Ru complex-catalyzed conversion of LA into 2-MTHF *via* GVL. It was found that the Cu/ZrO₂-OG catalyst obtained by 400 °C-calcination can deliver a remarkable conversion of GVL to give 2-MTHF in an excellent yield of *ca.* 91% within 6 h (Table 2, entry 2). Notably, this catalyst can be used at least three times with the yield of 2-MTHF from GVL remaining up to 85%. A high 2-MTHF yield could also be reached with the catalyst obtained by calcination at 300 °C (Table 2, entry 1). However, we found that the yield of 2-MTHF decreased dramatically to *ca.* 50% during the second use of the 300 °C-calcination derived catalyst. When the calcination temperature was further increased to 500 °C, only 65% yield of 2-MTHF was obtained under the same reaction conditions (Table 2, entry 3). Note that the Cu/ZrO₂-OG calcined at 700 °C can only afford a very poor yield of 2-MTHF (Table 2, entry 5). Thus the Cu/ZrO₂-OG catalysts obtained with relatively low calcination temperatures favor the selective formation of 2-MTHF *via* GVL hydrogenolysis at 240 °C.

To examine the reaction performed at 240 °C in detail, the product evolution for the hydrogenolysis of GVL with the 30 wt % Cu/ZrO₂-OG catalyst obtained by calcination at 400 °C was followed by continuous sampling using gas chromatography. As shown in Fig. 4, a mixture of 2-MTHF and 1,4-PDO as the main products in an approximate 3 : 1 ratio was produced at the initial stage of the reaction. In contrast to previous studies with selective γ -butyrolactone (GBL) transformation,²⁰ wherein the formation of THF from GBL was frequently found to proceed through a dual-step ring opening-dehydration sequence *via* intermediate formation of 1,4-butanediol,^{20c} it seems that the present Cu/ZrO₂-OG catalyst can deliver a facile reduction of the carbonyl moiety, thus enabling the direct formation of 2-MTHF in a more straightforward manner (Scheme 1, route **a**). Meanwhile, it is interesting to note that, with extension of the reaction time, the initially formed 1,4-PDO could be further converted into 2-MTHF.²¹ This indicates that, in parallel with the predominant formation of 2-MTHF *via* one-step direct carbonyl reduction of the GVL molecule as noted above, a small portion of 2-MTHF (*ca.* 10% yield) could also be progressively produced *via* the sequential pathway known for the selective hydrogenation of GBL.²⁰ This scenario is corroborated by the fact that

**Fig. 4** The time course of the conversion of GVL catalyzed by 400 °C-calcination-derived Cu/ZrO₂-OG. Conditions: GVL (5 mmol), catalyst (0.1 g), ethanol (10 mL), H₂ pressure (6 MPa), T (240 °C).

the dehydrative cyclization of 1,4-PDO to 2-MTHF over the 400 °C-calcination-derived Cu/ZrO₂-OG catalyst under identical reaction conditions was indeed possible (see Fig. S6, ESI†), albeit at a slower rate than in direct carbonyl reduction.

It was generally accepted that, besides the metal dispersion, the surface acidic sites in the Cu-based catalysts play a key role in the hydrogenolysis mechanism of lactone and a series of esters.²¹ To clarify the origin of the switchable catalytic activity of the Cu/ZrO₂-OG system as well as the high 2-MTHF yields achieved from GVL hydrogenolysis by using low temperature calcination-derived catalysts, an ammonia temperature-programmed desorption (NH₃-TPD) measurement was conducted. It is revealed that the 300 or 400 °C-calcined catalyst exhibits a higher abundance of weakly acid sites,²² as reflected from the significant desorption features appearing in the temperature region of 300–400 °C as seen in Fig. S5.† Carbon dioxide temperature-programmed desorption (CO₂-TPD) experiments have also been carried out to identify a possible influence of the surface basicity on the performance. However, it was found that there is only a weak relationship between the 2-MTHF yields and basic properties of the catalyst surface (not shown). This finding, together with the fact that a similar metallic copper dispersion has been identified for the several different Cu/ZrO₂-OG catalysts prepared by calcination at temperatures lower than 600 °C (Table S1, ESI†), indicates that a synergistic cooperation between dispersed Cu and the acid sites of the catalyst surface is essential to facilitate the direct reduction of the carbonyl group in the GVL molecule (Scheme 1, route **a**) or accelerate the subsequent dehydration of intermediate 1,4-PDO (Scheme 1, route **b**) to afford 2-MTHF.

In summary, we have demonstrated that a simple yet versatile heterogeneous catalyst system comprising Cu highly dispersed in a zirconia matrix can efficiently catalyze the selective hydrogenation of bio-derived GVL into valuable 1,4-PDO. Moreover, depending on the reaction conditions, it is possible to convert GVL to 2-MTHF in excellent yields using the same catalyst system with a slight modification of the preparation conditions.²³ More attractive applications for tunable valorization of these sustainable intermediates could be developed if a continuous

process using a fixed bed reactor could be implemented. The findings in this work could inspire the development of new economic and task-specific heterogeneous catalytic systems with superior performance in the flexible conversion of bio-derived platform molecules into higher value-added chemicals.

Acknowledgements

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