CHEMISTRY & SUSTAINABILITY

CHEM5U5CHEM

ENERGY & MATERIALS

Accepted Article

Title: Porous zirconium-furandicarboxylate microspheres for efficient redox conversion of biofuranics

Authors: Hu Li, Xiaofang Liu, Tingting Yang, Wenfeng Zhao, Shunmugavel Saravanamurugan, and Song Yang

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201601898

Link to VoR: http://dx.doi.org/10.1002/cssc.201601898



WILEY-VCH

www.chemsuschem.org

Porous zirconium-furandicarboxylate microspheres for efficient redox conversion of biofuranics

Hu Li,^[a] Xiaofang Liu,^[a] Tingting Yang,^[a] Wenfeng Zhao,^[a] Shunmugavel Saravanamurugan,^[b] Song Yang^[a]*

Abstract: Biofuranic compounds, typically derived from C5 and C6 carbohydrates, have been extensively studied as promising alternatives to fossil fule-based chemicals. The present work reports the simple assembly of bio-based 2,5-furandicarboxylic acid (FDCA) with different metal ions to prepare a range of metal-FDCA hybrids under hydrothermal conditions, which were demonstrated to have porous structure and acid-base bifunctionality. Especially, Zr-FDCA-T showed microspheric structure, high thermostability (ca. 400 °C), ampliative average pore diameters (ca. 4.7 nm), large density and moderate strength of Lewis base/acid centers (ca. 1.4 mmol/g) and few content of Bronsted acid sites, and was able to afford almost quantitative yields of biofuranic alcohols from corresponding aldehydes under mild conditions via catalytic transfer hydrogenation (CTH). Isotopic ¹H NMR and kinetic studies verified the direct hydride transfer to be the dominant pathway and rate-determining step of the CTH reactions. Importantly, the Zr-FDCA-T microspheres could be recycled with no decrease in catalytic performance and little leaching of active sites. Moreover, good yields of C5 (i.e., furfural) or C4 products (i.e., maleic acid and 2(5H)-furanone) could be obtained from furfuryl alcohol without oxidation of the furan ring over these renewable metal-FDCA hybrids. The content and ratio of Lewis acid/base sites were demonstrated to dominantly affect the catalytic performance of these redox reactions.

Introduction

Over the past decades, renewable lignocellulosic biomass has been explored to be the most abundant and promissing feedstock for producing biofuels and valuable chemicals ^[1]. In the presence of acidic catalysts, simultaneously coupled with basic/metallic sites, sugar and lignin components can be selectively converted to a wide range of products like polyols (e.g., sorbitol, mannitol, xylitol and ethylene glycol), organic acids (e.g., levulinic acid and lactic acid), furanic compounds (e.g., 5-hydroxymethylfurfural (HMF), 5-ethoxymethylfurfural (EMF), 2,5-dimethylfuran (DMF), 2,5-diformylfuran (DFF) and 2,5-furandicarboxylic acid (FDCA)), and phenolics (e.g., vanillin and veratraldehyde) ^[2]. Commonly, noble metal catalysts are

[a] Dr. H. Li, X. Liu, T. Yang, W. Zhao, Prof. S. Yang State-Local Joint Engineering Lab for Comprehensive Utilization of Biomass, State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering (Ministry of Education), Center for R&D of Fine Chemicals, Guizhou University Guiyang, Guizhou 550025, China E-mail: jhzx.msm@gmail.com

[b] Dr. S. Saravanamurugan Center of Innovative and Applied Bioprocessing (CIAB) Mohali 160 071, Punjab, India

Supporting information for this article is given via a link at the end of the document.

active for the valorization of biomass involving the processes of hydrogenation and oxidation ^[3]. Cheap transition-metal particles and oxides are deemed to be preferable candidates for both types of reactions, but they often suffer from some drawbacks such as need of harsh conditions, and relatively low stability and reusability ^[4].

Metal-organic frameworks (MOFs), which are typically composed of metal species and organic ligands to generate porous and crystalline polymers, have been illustrated to be most potentially applied in a variety of research fields such as substance separation, gas adsorption, sensing, energy storage and drug delivery^[5]. Particularly, an increasing attention has been placed on the use of MOFs containing flexible organic moieties and coordinatively unsaturated metal sites for heterogeneously catalyzing organic transformations and biomass conversions in recent years^[6]. To a great extent, the high surface areas and rich micropores of MOFs can significantly increase the contact probability of active sites to the substrates, especially for those dependent on shape selectivity^[7] However, the microporous network may on the other hand impede the access of bulky molecules to the cavities of MOFs^[8] and their thermal and chemical stability are relatively lower than most commercial solid materilas (e.g., zeolites)^[9], both of which probably inhibit the catalytic applications of MOFs in wide-range and large-scale production.

The development of functional and structural materials from natural composites has been considered to be one of important areas in material chemistry [10]. Starting from lignocellulose, a large number of porous carbonaceous materials prepared by calcination and grafted with different functional groups were demonstrated to show attractive prospects in catalysis, drug/gene delivery, and fuel cell [11]. As a more facile and controllable alternative to conventional preparative routes, the assembly of organic molecules derived from natural materials (e.g., phytic acid, polyphenol and porphyrin) with metal ions (e.g. Zr⁴⁺, Cu²⁺ and Fe³⁺) can not only mimic natural structures but also form a range of functions with enhanced stability ^[12]. Similar to the basic structure of terephthalic acid that is often used as organic ligand for MOFs preparation, FDCA has two -COOH groups at the para position of the ring, showing convenient replacement with each other in production of polymers ^[2f,2g]. Inspired by these grand findings, the present work is to design and prepare mesoporous acid-base bifunctional nanohybrids from bio-based FDCA and different metal ions under hydrothermal conditions for redox conversion of biofuranics in high efficiency. Moreover, studies on reaction parameters optimization, structure-activity relationship, catalyst recyclability, reaction mechanism, and catalytic kinetics are also carried out. To the best of our knowledge, this is the first report on the application of FDCA as a renewable organic ligand for

synthesizing acid-base bifunctional MOFs-type materials that can be used as stable and heterogeneous redox catalysts.

Results and Discussion

Catalyst charaterization

FT-IR spectra of ZrO₂, Zr-FDCA and Zr-FDCA-T in Fig. 1A show the characteristic of Zr-O bonds at 800 cm^{-1,[2e]} while the enhanced transmittance at wavenumbers of 1420 cm⁻¹ and 1610-1700 cm⁻¹ for both Zr-FDCA and Zr-FDCA-T reveals the symmetric and asymmetric stretching vibration of the -CO2 group, respectively ^[13]. A splitting of around 190 cm⁻¹ between these two peaks further indicates that the coordination mode of FDCA to Zr is bridging, rather than monodentate and bidentate modes (Fig.S1), which is consistent with the structure of UiO- $66(Zr)^{[14]}$. In the case of ZrO_2 , the bands at 1630 cm⁻¹ and 3450 cm⁻¹ are possibly belonged to water bending vibrations and the stretches of surface OH groups, respectively ^[2e]. The FT-IR spectra for Zr-FDCA and Zr-FDCA-T also exhibit a small broad peak at ~3200 cm⁻¹, which can contribute to the OH groups of monodentate FDCA molecules that may be incompletely coordinated to Zr by leaving some protonated carboxylic (-CO₂H) groups ^[14]. It should be noted that the use of CTAB and mesitylene as structure-directing agent for preparation of Zr-FDCA-T is most likely to enhance the binding ability of carboxylate to Zr, which can be well supported by its relatively weaker band at ~3200 cm⁻¹, as compared with Zr-FDCA.



FDCA-T

Fig. 1B illustrates the XRD patterns of ZrO₂, Zr-FDCA and Zr-FDCA-T. It can be seen that all these Zr-containing materials are amorphorous with only a few broad diffractions, although Zr-FDCA and Zr-FDCA-T have an obvious peak at 20 of ~7.5° with strong intensity, which is the typical (111) reflection of UiO-66(Zr) (Fig.S2) [15]. HR-TEM images of ZrO₂, Zr-FDCA and Zr-FDCA-T further confirm their poor crystalline structure (Fig. 2A-C). Fig. 2C shows the introduction of CTAB and mesitylene for Zr-FDCA-T preparation leading to the formation of wormlike feature, which may thus increase the surface area and porous structure despite the absence of lattice plane (Fig. 2D). Notably, the TEM and SEM images of Zr-FDCA-T demonstrate the slight aggregation of microspheres in nano size (80-120 nm; Fig. 2E-F), while the Zr, O and C compositions (i.e., Zr^{4+} and $-CO_2^{-}$ moities) in Zr-FDCA-T were evenly connected and dispersed, as observed from corresponding elemental mappings and STEM- HAADF (scanning transmission electron microscope and highangle annular dark-field) image in Fig. 3.



Fig.2. HR-TEM images of ZrO2 (A), Zr-FDCA (B) and Zr-FDCA-T (C), as well as TEM diffraction pattern (D), TEM image (E) and SEM image (F) of Zr-FDCA-T



Fig.3. STEM-HAADF image (a), and Zr (b), C (c) and O (d) elemental mappings of Zr-FDCA-T

Nitrogen adsorption-desorption isotherms of ZrO₂, Zr-FDCA and Zr-FDCA-T are shown in Fig. S3. The simultaneous presence of micro- and mesopores in ZrO₂ could be primarily resulted from the aggregate particles. Interestingly, the introduction of organic species (i.e., FDCA) was able to greatly increase the adsorbed quantity of N₂ and generate more centered distribution of mesopores, which might be the results of evenly assembled organic-inorganic networks (Fig. 3), especially in the case of Zr-FDCA-T. Table 1 collects the texture data of ZrO₂, Zr-FDCA, Zr-FDCA-T and UiO-66(Zr), including BET surface areas, pore volumes, and average pore diameters. UiO-66(Zr) has the highest surface area (1446 m²/g) and pore volume (0.61 m³/g), as shown in Table 1 and Fig. S4, while its pore dimension is only limited to microporous scale (1.7 nm). In contrast, Zr-FDCA and Zr-FDCA-T with much lower suface areas (ca. 200 m²/g) but show larger average pore sizes of 3.5 and 4.7 nm, respectively, which may facilitate the access of active sites to the substrate. For the amphoteric nature of the hybrids, it's interesting to find that Zr-FDCA and Zr-FDCA-T possess relatively higher

FULL PAPER

WILEY-VCH

hydrophobicity than neat ZrO₂, which can be well supported by the contact angles of a water droplet on their surfaces (Fig. 4 & Fig.S5) ^[16]. This character of Zr-FDCA and Zr-FDCA-T can further confirm the even connection of zirconium and carboxylate species with less free protonated $-CO_2H$ groups, which is in agreement with the results of FT-IR (Fig. 1A) and elemental mappings (Fig. 3).

Table 4 Tayture and said base	properties of 7r containing actaluate
Table I. Texture and actu-base	

Catalyst	S _{BET} (m²/g) ^[a]	V _{pore} (m ³ /g) ^[b]	D _{pore} (nm) ^[c]	Basicity (mmol/	Acidity (mmol/	Base/ acid			
				g) ^[a]	g) ^[0]	ratio			
Zr-FDCA	170	0.15	3.5	0.80	0.67	1:0.8			
Zr-FDCA-T	207	0.24	4.7	0.79	0.59	1:0.7			
ZrO ₂	86	0.12	5.5	0.37	0.34	1:0.9			
UiO-66(Zr)	1446	0.61	1.7	0.69	0.77	1:1.1			

^[a] BET surface area was determined by N₂ adsorption isotherm.

^[b] Pore volume was estimated by BJH adsorption cumulative volume of pores.

^[c] Adsorption average pore diameter (4V/A by BET).

^[d] Basicity and acidity was determined by NH₃- and CO₂-TPD, respectively.



Fig.4. Contact angle (CA) of a water droplet on the surface of Zr-FDCA (A) and Zr-FDCA-T (B) $\,$

Prior to determining the basicity (derived from O species in the framework of M-O-C) and acidity (from metal and -COOH moieties) of the metal-FDCA hybrids, the thermal stability of selected Zr-FDCA and Zr-FDCA-T samples was initially measured by TG analysis. Fig. 5A clearly demonstrates that both Zr-FDCA and Zr-FDCA-T hybrids are not decomposed until the temperature reaches to 400 °C. In order to obtain the accurate results of acid/base site contents for these solid bybrids by using NH₃/CO₂-TPD, the maximum desorption temperature was set at 300 °C (Figs. S6-S7). The basicity and acidity of different metal-FDCA hybrids (i.e., AI-FDCA, Cr-FDCA, Fe-FDCA, Cu-FDCA, and Zr-FDCA) were supplied in Table S1, wherein the type of metal ions was found to significantly affect the base/acid site distribution and contents, as well as their strength that can be directly evaluated on the basis of the desorption temperature ^[17]. In the case of Zr-containing catalysts, the inroduction of the organic species FDCA assembled with Zr

was most likely to promote the formation of more acid and base sites, as compared with neat ZrO_2 (Table S1, Table 1). More interestingly, the assembly of Zr with FDCA for preparing Zr-FDCA and Zr-FDCA-T hybrids could increase the contents of Lewis acid sites (coordinated Zr; 1430-1450 cm⁻¹) through consuming Bronsted acid sites (free –COOH; 1530-1545 cm⁻¹), to some extent, as proved by pyridine-adsorbed FT-IR spectra (Fig. 5B).



Fig.5. TG curves (A) and pyridine-adsorbed FT-IR spectra (B) of Zr-containing catalytic materials

CTH of FUR to FFA with different catalysts

Furfural (FUR) is one of important components in bio-oils, which is generally derived from C5 sugars via dehydration under hydrothermal conditions ^[18]. However, the –CHO groups in FUR are susceptible to be condensed to humins, and much attention has been thus laid on the stabilization of FUR by selective hydrogenation to furfuryl alcohol (FFA) over noble metals (e.g., Pt, Pd and Ru) [19]. Therefore, CTH of FUR to FFA in 2-PrOH was initially chosen to examine the catalytic performance of different metal-FDCA hybrids (Table 2). Almost no reaction took place in the absence of any catalyst at 140 °C after 4 h (entry 1). With the addition of metal-FDCA catalyst (i.e., AI-FDCA, Cr-FDCA, Fe-FDCA, and Cu-FDCA) into the reaction system, low FFA yields (1–14%) along with even more downstream products including 2-(isopropoxy)methyl furan (IPMA; 2-19% yields) and isopropyl levulinate (IPL; 5-8% yields) were observed (entries 2-5). The existence of more acid sites with high strength (base/acid site ratio: 1/2.4-1/11.6; Table S1) in these metal-FDCA hybrids seemed to promote further etherification of FFA to IPMA and even alcoholysis to give IPL (Scheme S1), while the lack of enough base sites that are favorable for the process of hydrogen tranfer (HT) failed to catalyze FUR being converted to FFA in high efficiency ^[16].

Table 2. CTH of FUR to FFA with ZrO ₂ , UiO-66(Zr) and metal-FDCA hybrids ^[a]									
Entry	Catalyst	FFA yield(%)	FFA selec.(%)	FUR conv.(%)	TOF (h ⁻¹) ^[b]	10 ⁻⁶ × <i>k</i> (s⁻¹) ^[c]	IPMA yield(%)	IPL yield(%)	
1	Blank	0	0	<2		1.4			
2	AI-FDCA	14	36	39	0.7	34.3	14	7	
3	Cr-FDCA	3	17	18	0.2	13.8	5	6	
4	Fe-FDCA	13	28	47	0.7	44.1	19	8	
5	Cu-FDCA	<1	10	9	<0. 1	6.5	2	5	
6	Zr-FDCA	78	94	83	2.7	123.1	3	<1	
7	Zr-FDCA-T	96	98	98	3.5	271.7	1	<1	
8	ZrO ₂	41	79	52	2.9	50.9	8	2	
9	UiO-66(Zr)	72	84	86	2.5	136.5	3	<1	

[a] Reaction conditions: 2 mmol FUR, 0.1 g catalyst, 10 mL 2-PrOH, T = 140 °C, and t = 4 h. [b] TOF = (mole of FFA) / (mole of acid/base sites × time). [c] Reaction rate constant k is obtained from $-\ln(1 - FUR \text{ conversion})$ vs time ^[18b]. FFA: furfuryl alcohol; FUR: furfural; IPMA: 2-(isopropoxy)methyl furan; IPL: isopropyl levulinate



Gratifyingly, Zr-FDCA had more weak base sites (i.e., 0.63 and 0.17 mmol/g centered at the desorption temperature of 94 and 280 °C, respectively) and comparable density of acidic sites in weak to moderate strength (i.e., 0.54 and 0.13 mmol/g centered at the desorption temperature of 116 and 269 °C, respectively) to other metal-FDCA hybrids (Scheme S1), and was able to catalyze FUR being transformed to FFA in a relatively higher yield of 78% with an enhanced TOF (2.7 h⁻¹) which was 4-27 times higher than that of AI-FDCA, Cr-FDCA, Fe-FDCA and Cu-FDCA (0.1-0.7 h⁻¹; Table 2, entries 2-6). Further modification of Zr-FDCA (base/acid ratio 1:0.8) with CTAB to prepare Zr-FDCA-T microspheres (Fig. 2F) bearing an increased surface area and pore size (Table 1) could ulteriorly accelerate the base/acid site ratio to 1:0.7 (Table S1). As a result, the optimal Zr-FDCA-T hybrid afforded a much higher FFA yield (96%), and TOF (3.5 h⁻ ¹) and k (2.7 × 10⁻⁴ s⁻¹) increased by a magnitude of 1.3 and 2.2 times, respectively, as compared with Zr-FDCA (Table 2, entries 6 & 7). In contrast, either ZrO_2 with lower surface area (86 m²/g) and base/acid site contents (0.37 and 0.34 mmol/g) or UiO-66(Zr) with smaller average pore diameter (1.7 nm; Table 1) showed inferior activity to Zr-FDCA-T (Table 2, entries 7-9). These results clearly demonstrate that the content of base/acid sites in an appropriate molar ratio, surface area, and pore size are all positively correlated with the pronounced performance of the catalyst.



It was also not difficult to find that UiO-66(Zr) having micropores centered at 1.7 nm could still give a moderate FFA yield of 72% from CTH of FUR, which was comparable to that obtained over Zr-FDCA (78%) and higher than ZrO₂ (41%), respectively (Table 2). Apart from the promotional effect of larger suface area (1446 m^{2}/g) and comparable base/acid sites (0.69 and 0.77 mmol/g in a ratio of 1/1.1) to Zr-FDCA-T (Table 1), the strength of acid and base sites could be another crucial factor in affecting CTH of FUR to FFA ^[12d]. To elucidate this speculation, Zr 3d and O 1s in ZrO₂, Zr-FDCA, Zr-FDCA-T and UiO-66(Zr), separately corresponding to Lewis acid and base centers, were recorded with XPS (Fig. 6). A higher Zr 3d binding energy means a larger positive charge of Zr species, thus indicating the Zr centers to have much stronger Lewis acidity (Fig. 6A) ^[20]. In turn, a lower O 1s binding energy illustrates a higher negative charge and basicity of oxygen in C-O-Zr (Fig. 6B) [8c]. Therefore, the Lewis acidity and basicity of these catalysts are in the order of Zr-FDCA-T > UiO-66(Zr) > Zr-FDCA > ZrO₂ and Zr-FDCA > Zr- $FDCA-T > ZrO_2 > UiO-66(Zr)$, respectively. Besides high contents and appropriate molar ratios of acid/base sites, the predominant acidity but low to moderate base strength of ZrFDCA-T and UiO-66(Zr) could be concluded to be also helpful for selective production of FFA from FUR by getting rid of forming condensation products from either FUR or FFA mediated by strong base ^[16].

It's worth noting that the in situ generated acetone from 2-PrOH during CTH of FUR with Zr-FDCA-T was much less than that from pure 2-PrOH, which is in good agreement with a previous report ^[21]. As compared with 2-PrOH, FUR seemed to show superior availability to the relatively hydrophobic surface of Zr-FDCA-T (Fig. 4), which could also be verified by the adsorption energy of FUR (-2.4 eV) > FFA (-1.8 eV) > acetone (-1.1 eV) > 2-PrOH (-1.0 eV) [22], thus significantly restraining the dehydrogenation rate of 2-PrOH during the CTH system. Notably, Zr-FDCA-T exhibited comparable and even higher catalytic performance in CTH of FUR to FFA (Table S2), as compared with noble and transition metal particles (e.g., Pt, Cu, Ni, Co, and Fe) by using either H₂ or alcohol as hydrogen-donor (H-donor)^[23]. These results demonstrate that porous acid-base bifunctional Zr-FDCA-T simply prepared from the assembly of bio-based molecule FDCA with Zr display promising applications in CTH reactions.

Effect of reaction temperature and time on CTH of FUR

In the presence of the Zr-FDCA-T microshperes, the effect of reaction temperature (i.e., 80, 100, 120, 140, and 160 °C) on product distribution in CTH of FUR was further investigated after reacting for 4 h (Fig. 7A). At a relatively low temperature of 80 °C IPMA (12% yield) formed by etherification of FFA with 2-PrOH was found to be the major byproduct during CTH of FUR, implying that etherification and transfer hydrogenation of 2-PrOH are most likely to be two competitive reactions. With the increase of reaction temperature from 80 to 140 °C, the yield of IPMA gradually decreased to aound 1%, which clearly indicated the acceleration of relatively high temeprature (i.e., 140 °C) on the transfer hydrogenation process for selective production of FFA from FUR (Fig. 7A). When the reaction temeprature further increased to 160 °C, the downstream product (i.e., IPL) derived from IPMA was observed to be the dominant byproduct, as identified by GC-MS in Fig.S8. Therefore, it can be unambiguously perceived that a relatively high temperature of 140 °C is more favorable for the exclusive formation of FFA from FUR in 2-PrOH.



Fig.7. CTH of FUR to FFA at different reaction temperatures after 4 h (A) and in different reaction times at 140 °C (B); Reaction conditions: 2 mmol FUR, 0.1 g Zr-FDCA-T, and 10 mL 2-PrOH.

In line with the effect of reaction temperature on product distribution in CTH of FUR to FFA, either IPMA or IPL was found to be primarily formed as the byproduct in yields of up to 7%, by varying reaction time in the range of 0.5–10 h at 140 °C (Fig. 7B). IPMA seemed to be not stable after long reaction duration (≥4 h), which could be reversibly converted to FFA, or further transformed into IPL. However, a certain amount of unkown propducts (<5% in total) was formed after reacting for 10 h, which was possibly caused by some FFA-involved side reactions like oligomerization and condensation ^[24]. The optimized reaction time (4 h) and temeprature (140 °C) were thus selected and used for the subsequent studies.

Catalyst recyclability in CTH of FUR to FFA

Prior to the recycling study of Zr-FDCA-T, the effect of catalyst dosage on CTH of FUR to FFA was initially examined (Fig. 8A). It was interesting to note that the selectivity toward FFA increased from 63% to 98% with the addition of more Zr-FDCA-T (25-100 mg). During these catalytic processes, the hemiacetalization of FUR with 2-PrOH was found to be the dominant reaction route to consume the substrate ^[22], thus resulting in low to moderate FFA selectivities at relatively high FUR conversions by using relatively low catalyst dosages (25-75 mg). Although Zr-FDCA-T with a large dosage of 200 mg could promote the complete conversion of FUR (Fig. 8A) without producing the hemiacetal byproduct, the downstream products of FFA (e.g., IPMA and IPL) catalyzed by excess acid and base sites were formed instead.



Fig.8. Effect of Zr-FDCA-1 dosage on FUR-to-FFA conversion at 140 °C for 4 h (A), and catalytic behavior study of Zr-FDCA-T in FUR-to-FFA conversion at 140 °C by varying reaction time (B)

To study the catalytic behavior of Zr-FDCA-T for CTH of FUR to FFA in 2-PrOH at 140 °C, two parallel experiments by using the solid catalyst in an optimal dosage of 100 mg with or without separating the catalyst from the hot reaction mixture after 1 h were conducted (Fig. 8B). After stirring for another 5 h under identical conditions, Zr-FDCA-T could smoothly catalyze FUR being converted to FFA, while almost no reaction was observed to take place for the reaction system being filtered out the catalyst. ICP-OES analysis showed both filtrates containing <1 ppm of zirconium species, clearly manifesting the intactness and heterogeneous catalysis of Zr-FDCA-T in the CTH reactions.

The reusability of a solid catalyst is one of important indexes to evaluate its potential application in industrial production ^[25]. Over six consecutive cycles, Zr-FDCA-T could be simply recovered by washing with DMF and ethanol, and capable of producing FFA

in yields of 91-96% at almost complete FUR conversions under the optimized reaction conditions (Fig. S9). At relatively low FUR conversions of around 50%, Zr-FDCA-T was also able to catalyze FUR being converted to FFA with a slight decrease in yields by no more than 4% after five cycles (Fig.S10). These results confirmed the robust active sites and high durability of Zr-FDCA-T in CTH of FUR to FFA.

To accurately investigate the structural changes in Zr-FDCA-T before and after CTH reactions for six cycles, a variety of characterization techniques including TG analysis, nitrogen adsorption-desorption, pyridine-adsorbed FT-IR, CO2-TPD, FT-IR, XRD, and SEM have been adopted (Fig. 9, Figs.S11-S13). A slight reduction of surface area (from 207 to 185 m²/g) was detected (Fig. 9A), which could be ascribed to the adsorption of organic species into cavities of Zr-FDCA-T during the reactions (Fig. 9B, Fig.S11). Only minor leaching of Zr species (~3% of total Zr content) was observed, as determined by ICP-OES analysis. Although the total acidity of Zr-FDCA-T was almost in constant contents of 0.55-0.59 mmol/g after recycling for six times, the distribution of Lewis and Bronsted acid sites was changed a little bit by consuming the former ones to generate the latter (Fig. 9C). The slightly increased intensity of the adsoption at around 3200 cm⁻¹ for reused Zr-FDCA-T could be assigned to the in situ formed OH groups of monodentate FDCA molecules (Fig.S12), implying the possible dissociation of coordinated Zr and carboxylate groups to liberate -CO₂H, to a small degree. Surprisingly, the basicity of the reused Zr-FDCA-T increased by about 0.1 mmol/g (Fig. 9D), which might be resulted from the adsorbed basic organic species (e.g., 2propoxide) and the generated rough surfaces of the recovered catalyst (Fig.S13) to facilitate the access of CO₂ by TPD analysis



Fig.9. Nitrogen adsorption-desorption isotherms (A), TG curves (B), pyridineadsorbed FT-IR spectra (C), and CO_2 -TPD patterns of fresh and reused Zr-FDCA-T microspheres for six cycles

CTH of other biofuranics and selected deuterium labeling experiments

Encouraged by the predominant catalytic performance of Zr-FDCA-T microspheres in CTH of FUR to FFA, other biofuranics including 5-hydromethylfurfural (HMF) and 5-methylfurfural (MF) derived from C6 sugars have also been used as substrates to produce corresponding alcohols 2,5-bis(hydroxymethyl)furan (BHMF) and 5-methylfurfuryl alcohol (MFA). High yields of BHMF (87%) and MFA (95%) at almost complete substrate conversions could be achieved at 140 °C after reacting for 8 and 6 h, respectively (Table S3).

To elucidate the reaction mechanism, CTH of HMF to BHMF in 2-PrOH (d₈) was monitored at varying times by ex situ nuclear magnetic resonance (NMR) spectrometer (JEOL-ECX 500), as shown in Fig. 10. The obtained ¹H NMR spectra show the proton in aldehyde group (i.e., -CHO) of HMF (1a) gradually disappeared by increasingly adding deuterium (D) from 2-PrOH (d_8) to its C=O bond. Accordingly, the methylene (-CH₂-) and methine (-CH-) groups of HMF were separately shifted to 2b and 1b in D-labeled BHMF (Fig. 10). GC-MS spectrum for CTH of HMF in 2-PrOH (d_8) illustrates the formed BHMF having two almost equivalent molecular ion peaks with additional 2 and 3 amu (i.e., m/z = 130 and 131), respectively (Fig.S14), which can be caused by the direct hydrogen transfer and proton exchange between HMF and 2-PrOH (d₈) in the column during GC-MS analysis (Scheme S2) [16]. The reaction rate of HMF-to-BHMF conversion in normal $(k_{\rm H})$ and isotopic $(k_{\rm D})$ 2-PrOH was indepentently determined under identical conditions, and the $k_{\rm H}/k_{\rm D}$ value was found to be 2.1. These unequal rate constants further proved the CTH reaction proceeding through the direct hydride transfer as the rate-determining step [26].



Fig.10. ¹H NMR spectra of HMF-to-BHMF conversion in isotopic 2-PrOH (d_8) at varying times

Catalytic oxidation of furfuryl alcohol

In addition to the hydrogenation reactions, catalytic oxidations of FFA with H_2O_2 over different metal-FDCA hybrids were also investigated at 45 °C for 2 h, and the results are shown in Table S4. It was reported that a range of C4 compounds (e.g., maleic acid and 2(5H)-furanone), acetic acid, and humins would be formed in H_2O_2 -mediated oxidation of FUR owing to the

simultaneous presence of oxidizable C=C and C=O groups ^[27]. In this study, all metal-FDCA hybrids were demonstrated to significantly suppress the furan ring oxidation. Notably, Zr-FDCA-T with moderate Lewis basicity and acidity could selectively catalyze FFA being incompletely oxidized to FUR (up to 41% yield), while Cr-FDCA and Cu-FDCA with superior Lewis acidity afforded high yields of maleic acid and 2(5H)-furanone (~60% in total). These results further confirmed the role of acid and base sites in controlling the distribution of products derived from furanic compounds via redox reactions.

Conclusions

A range of porous acid-base bifunctional metal-FDCA hybrids (i.e., Cr-FDCA, Cu-FDCA, AI-FDCA, Fe-FDCA, Zr-FDCA, and Zr-FDCA-T) were successfully prepared from simple assembly of bio-based FDCA with corresponding metal ions under hydrothermal conditions, and demonstrated to be highly efficient for redox conversions of biofuranics without breaking C=C bond of the furan ring. In the presence of Zr-FDCA-T microspheres, CTH of biofuranic aldehydes to corresponding alcohols could be achieved with almost quantitative yields, and the direct hydride transfer was verified to be the dominant reaction pathway and the rate-determining step by isotopic ¹H NMR and kinetic studies Importantly, Zr-FDCA-T microspheres were able to be reused with no significant decrease in catalytic activity and little leaching of active sites. Moreover, these metal-FDCA hybrids were also found to show high selectivity in catalytic oxidation of FFA to either C5 or C4 products with moderate yields. This type of biobased functional catalysts shows great potential in organic synthesis and biomass valorization, and the simple preparation methods may be used for developing other renewable catalytic materials.

Experimental Section

Materials

2,5-Furandicarboxylic acid (FDCA, 98%), *p*-phthalic acid (99%), zirconium chloride (ZrCl₄, ≥99.5%), aluminum chloride (AlCl₃, 99%), chromium chloride hexahydrate (CrCl₃·6H₂O, 98%), iron chloride (FeCl₃, 98%), copper chloride (CuCl₂, 98%), hexadecyl trimethyl ammonium bromide (CTAB, 99%), hydrogen peroxide solution (30 wt% H₂O₂ in water), 2-propanol (99.5%) and *N*,*N*-dimethylformamide (DMF, 99.8%) were brought from Aladdin Industrial Inc. (Shanghai). Furfural (FUR, 99%), furfuryl alcohol (FFA, 98%), 5-methylfurfural (MF, 99%), 5-methylfurfuryl alcohol (MFA, 97%), 5-hydroxymethylfurfural (HMF, 99%), 2,5-bis(hydroxymethyl)furan (BHMF, 98%), 2(5H)-furanone (98%), maleic acid (MA, 99%), mesitylene (>98%), and 2-propanol-*d*₈ (2-PrOH-*d*₈, 99.5 atom% D) were purchased from J&K Scientific Ltd. (Beijing). All other reagents (analytical grade) were utilized as recieved without any treatment, unless otherwise mentioned.

Catalyst preparation

All metal-biofuranic catalysts (M-FDCA; M = Zr, Al, Cr, Fe, and Cu) were prepared from the self-assembly of 2,5-furandicarboxylic acid (FDCA)

FULL PAPER

with equivalent corresponding metal chloride (i.e., ZrCl₄, AlCl₃, CrCl₃, FeCl₃, or CuCl₂) in DMF under hydrothermal conditions. In a typical procedure, 1.5 mmol FDCA (0.23 g) and 1.5 mmol ZrCl₄ (0.35 g) were dissolved in 15.5 mL DMF (0.2 mol) in a 25 mL teflon-lined stainless steel autoclave by stirring at room temperature for 10 min. The tightly sealed autoclave was kept in an oven (JZ-4-1200, Shanghai Jingzhao Mechanical Equipment Co. Ltd.) under static conditions at 120 °C for 24 h. Upon completion, the resulting white precipitates were filtered out and successively washed with DMF and ethanol for 5-8 times until colorless transparent filtrate was observed, followed by drying at 100 °C overnight to afford the target sample Zr-FDCA. To further extend the aperture structure of Zr-FDCA, CTAB (0.45 mmol) and mesitylene (0.45 mmol) were added as co-reagents under other identical conditions, and the obtained material was denoted as Zr-FDCA-T. For comparison, ZrO₂ (calcined at 150 °C for 12 h) and UiO-66(Zr) were also synthesized, according to previously reported procedures [28].

Catalyst characterization

Wide angle XRD (X-ray diffraction) patterns in a range of 5-90° were recorded on a D8 Advance X-ray powder diffractometer with a Cu Ka radiation source (Bruker, Germany). FT-IR (Fourier transform-infrared) spectroscopy was conducted using a Nicolet 6700 spectrometer (Thermo Fisher Scientific, US) in a thin KBr disk. Pyridine adsorbed FT-IR spectra were measured with a Bruker VERTEX V70v system, wherein a temperature-programmed desorption of pyridine-adsorbed sample at 250 °C for 1 h (from 25 °C with a heating ramp of 5 °C min⁻¹) was implemented before FT-IR analysis. SEM (scanning electron microscopy; MERLIN Compact, ZEISS, Germany) and HR-TEM (high resolutiontransmission electron microscope; Tecnai G2 F20, FEI, US) were used to the morphologies of catalytic materials. STEM-HAADF (Scanning transmission electron microscope and high-angle annular dark-field) imaging was obtained from an aberration corrected (S)TEM (JEM-1200EX, JEOL, Japan) fitted with energy dispersive X-ray (EDX). BET (Brunauer-Emmett-Teller) surface area, BJH pore size and volume were measured with nitrogen physisorption (JW-BK132, JWGB Sci & Tech Co. Ltd., Beijing) at liquid nitrogen temperature. TG (thermogravimetry) analysis was taken with a DTG-60AH instrument (Shimadzu, Japan) under N₂ atmosphere (40 mL/L) at a temperature range of 25-600 °C in a heating ramp of 5 °C/min. XPS (X-ray photoelectron spectroscopy) was operated using a K-Alpha instrument (Thermo Fisher Scientific, US). The contact angle of a water droplet on the solid sample surface was determined at room temperature by using a DSA30 instrument (Kruss, Germany). NH₃- and CO₂-TPD (temperature programmed desorption) patterns were recorded with an AutoChem II 2920 chemisorption analyzer (Micromeritics, US) to evaluate the surface acidity and basicity of catalytic materials, respectively. Before analyzing the gas (i.e., NH₃ or CO₂) desorption with a thermal conductivity detector (TCD) every one second at programmed temperature from 50 to 300 °C in He (with a heating ramp of 10 °C min⁻¹ and keeping at 300 °C for 60 min), the solid sample in a quartz reactor was initially decassed at 150 °C for 60 min. and then flushed with 10% NH₃ or CO₂ in 90% He (60 mL/min) for 60 min to enable the complete adsorption of NH₃ or CO₂ at 50 °C, followed by flushing with pure He (60 mL min⁻¹) for another 60 min to elute the gas physically adsorbed to the solid material.

Catalytic transfer hydrogenation (CTH) of bio-based carboxides

CTH reactions of bio-based carbonyl compounds with 2-propanol (2-PrOH) were all conducted in a 15 mL Ace pressure tube (Synthware, Beijing) under oil-heating conditions. In a general procedure, 2.0 mmol furfural (FUR), 0.1 g catalyst, and 10 mL 2-PrOH were added into the reactor, and then placed into the preheated oil bath at a desired temperature of 80-160 $^{\circ}$ C, followed by magnetically stirring for a specific reaction time (i.e., 0.5-10 h) at 600 rpm. Upon completion, the tube was quenched by cold water in a beaker, and the liquid mixture was quantitatively analyzed by gas chromatography (GC).

Catalytic oxidation of furfuryl alcohol

To a 15 mL Ace pressure tube, 1 mmol furfuryl alcohol (FFA), 2 mL 30 wt% H_2O_2 , and 0.05 g catalyst were added. The resulting mixture was then put into the oil bath under vigorously stirring, and heated to 45 °C for 2 h. After the reaction, the aqueous solution was quantitatively analyzed by high performance liquid chromatography (HPLC).

Catalyst recycling

For recycling the catalyst, the solid residue in the solution after each cycle was separated by centrifugation, successively washed with DMF and ethanol for 5 times, dried at 120 °C for 5 h, and directly employed for the next run. To examine the leaching content of active species, the reaction mixture after filtering out the catalyst and volumetrically diluting with deionized water was sent for ICP-OES (inductively coupled plasma-optical emission spectroscopy) analysis with a PerkinElmer Optima 8000 instrument.

Sample analysis

To identify the products after reactions, the resulting mixtures were diluted with methanol and analyzed by GC-MS (Agilent 6890N GC/5973 MS, US). FUR, FFA, and other reagents and products involved in CTH reactions were quantitatively analyzed on GC (Agilent 7890B) with a flame ionization detector (FID) and a HP-5 column (30 m × 0.320 mm × 0.25 µm) by using naphthalene as internal standard. The substrate conversions and product yields were calculated on the basis of the standard curves of commercial or isolated (i.e., IPMA and IPL) samples. For quantitative analysis of products in aqueous solution, HPLC (LC-20A, Shimadzu, Kyoto) was used instead, which was fitted with an Aminex HPX-87H column, and ultraviolet and refractive index detectors.

Acknowledgements

We wish to thank the financial supports from the National Natural Science Foundation of China (21576059 & 21666008), and the National Key Technologies R&D Program of China (2014BAD23B01).

Keywords: Renewable materials • biofuranic compounds • heterogeneous catalysis • acid-base bifunctionality • biomass

a) A. Corma, S. Iborra, A. Velty, *Chem. Rev.* 2007, 107, 2411-2502; b) P. Gallezot, *Chem. Soc. Rev.* 2012, 41, 1538-1558; c) J. M. Galazka, J. H. D. Cate, *Energy Environ. Sci.* 2011, 4, 3329-3333; d) H. Li, Z. Fang, R. L. Smith Jr., S. Yang, *Prog. Energ. Combust.* 2016, 55, 98-194; e) D. M. Alonso, S. G. Wettstein, J. A. Dumesic, *Chem. Soc. Rev.* 2012, 41, 8075-8098.

^[2] a) H. Li, P. S. Bhadury, A. Riisager, S. Yang, Catal. Sci. Technol. 2014, 4, 4138-4168; b) W. Deng, Q. Zhang, Y. Wang, Catal. Today 2014, 234, 31-

FULL PAPER

WILEY-VCH

41; c) H. Li, S. Yang, A. Riisager, A. Pandey, R. S. Sangwan, S Saravanamurugan, R. Luque, Green Chem. 2016, 18, 5701-5735; d) S. Kang, X. Li, J. Fan, J. Chang, Renew. Sustain. Energy Rev. 2013, 27, 546-558; e) H. Li, Z. Fang, J. Luo, S. Yang, *Appl. Catal. B: Environ.* **2017**, *200*, 182-191; f) X. Han, C. Li, X. Liu, Q. Xia, Y. Wang, *Green Chem.* **2017**, DOI: 10.1039/c6gc03304k; g) Z. Zhang, K. Deng, ACS Catal. 2015, 5, 6529-6544.

- [3] a) M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.* 2014, *114*, 1827-1870; b)
 J. Ohyama, Y. Hayashi, K. Ueda, Y. Yamamoto, S. Arai, A.Satsuma, *J. Phys. Chem. C* 2016, *120*, 15129-15136; c) J. Lee, Y. Xu, G. W. Huber, Appl. Catal. B: Environ. 2013, 140-141, 98-107; d) C. Ortiz-Cervantes, M.
- Appl. Catal. B: Environ. 2013, 140-141, 98-107, 0) C. Ortiz-cervantes, M. Flores-Alamo, J. J. García, ACS Catal. 2015, 3, 1424-1431; e) X. Li, W. Wan, S. Kattel, J. G. Chen, T. Wang, J. Catal. 2016, 344, 148-156.
 [4] a) The American Ceramic Society (2009) Synthesis of nanophased metal oxides in supercritical water: Catalysts for biomass conversion, in Progress in Nanotechnology, John Wiley & Sons, Inc., Hoboken, NJ, USA; b) X. Tang, H. Chen, L. Hu, W. Hao, Y. Sun, X. Zeng, L. Lin, S. Liu, Appl. Catal. 2016, 147, 292, 2924; b) Yang, J. Chei, Y. Liu, Appl. Catal. B: Environ. 2014, 147, 827-834; c) K. Yan, Y. Yang, J. Chai, Y. Lu, Appl. Catal. B: Environ. 2015, 179, 292-304.
- [5] a) H. C. J. Zhou, S. Kitagawa, Chem. Soc. Rev. 2014, 43, 5415-5418; b) Y. He, W. Zhou, G. Qian, B. Chen, *Chem. Soc. Rev.* 2014, *43*, 5657-5678; c)
 P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G.
 Férey, R. E. Morris, C. Serre, *Chem. Rev.* 2012, *112*, 1232-1268; d) J. Liu,
 L. Chen, H. Cui, J. Zhang, L. Zhang, C. Y. Su, *Chem. Soc. Rev.* 2014, *43*, 5982-5993; f) Y. S. Bae, R. Q. Snurr, Angew. Chem. Int. Ed. 2011, 50, 11586-11596.
- [6] Z. J. Lin, J. Lü, M. Hong, R. Cao, *Chem. Soc. Rev.* 2014, 43, 5867-5895.
 [7] a) J. Gascon, A. Corma, F. Kapteijn, X. Llabres, *ACS Catal.* 2013, 4, 361 [7] J. O. Gustan, M. Gonta, T. Araha, J. Roberts, K. A. Scheidt, Z. Stere, S. B. Stere, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* 2009, *38*, 1450-1459; c) D. Y. Hong, Y. K. Hwang, C. Serre, G. Ferey, J. S. Chang, *Adv. Funct. Mater.* 2009, *19*, 1537-1552.
 [8] a) Z. Zhang, M. J. Zaworotko, *Chem. Soc. Rev.* 2014, *43*, 5444-5455; b) W. Xuan, C. Zhu, Y. Liu, Y. Cui, *Chem. Soc. Rev.* 2012, *41*, 1677-1695; c) H. Liu, Y. Liu, Y. Liu, Y. Cui, *Chem. Soc.* Rev. 2012, *41*, 1677-1695; c) H.
- Li, Z. Fang, J. He, S. Yang, ChemSusChem, **2017**, DOI: 10.1002/cssc.201601570
- [9] a) G. Ferey, *Chem. Soc. Rev.* 2008, 37, 191-214; b) A. H. Valekar, K. H.
 Cho, S. K. Chitale, D. Y. Hong, G. Y. Cha, U. H. Lee, D. W. Hwang, C.
 Serre, J. S. Chang, Y. K. Hwang, *Green Chem.* 2016, *18*, 4542-4552.
 [10] a) U. G. K. Wegst, H. Bai, E. Saiz, A. P. Tomsia, R. O. Ritchie, *Nature*
- Mater. 2015, 14, 23-36; b) E. Munch, M. E. Launey, D. H. Alsem, E. Saiz, A. P. Tomsia, R. O. Ritchie, Tough, bio-inspired hybrid materials, Science 2008, 322, 1516-1520.
- [11] a) P. Zhang, Y. Gong, H. Li, Z. Chen, Y. Wang, Nature Commun. 2013, 4, [11] G. D. Kai, M. J. Tan, P. L. Chee, Y. K. Chua, Y. L. Yap, X. J. Loh, *Green Chem.* **2016**, *18*, 1175-1200; c) V. Veeramani, R. Madhu, S. M. Chen, B. S. Lou, J. Palanisamy, V. S. Vasantha, *Sci. Rep.* **2015**, *5*, 10141.
 [12] a) J. Guo, Y. Ping, H. Ejima, K. Alt, M. Meissner, J. J. Richardson, Y. Yan,
- K. Peter, D. von Elverfeldt, C. E. Hagemeyer, F. Caruso, Angew. Chem. Int.

Ed. 2014, 53, 5546-5551; b) J. O. Alben, P. P. Moh, F. G. Fiamingo, R. A. Altschuld, Proc. Natl. Acad. Sci. USA 1981, 78, 234-237; c) S. Narute, R. Parnes, F. D. Toste, D. Pappo, J. Am. Chem. Soc. 2016, 138, 16553-16560; d) J. Song, B. Zhou, H. Zhou, L. Wu, Q. Meng, Z. Liu, B. Han, Angew. Chem. Int. Ed. **2015**, *54*, 9399-9403.

- [13] F. Verpoort, T. Haemers, P. Roose, J. P. Maes, Appl. Spectrosc. 1999, 53, 1528-1534
- [14] K. B. Lausund, O. Nilsen, Nature Commun. 2016, 7, 3578.
 [15] G. C. Shearer, S. Chavan, S. Bordiga, S. Svelle, U. Olsbye, K. P. Lillerud, Chem. Mater. 2016, 28, 3749-3761.
- [16] H. Li, J. He, A. Riisager, S. Saravanamurugan, B. Song, S. Yang, ACS Catal. 2016, 6, 7722-7727
- [17] S. Saravanamurugan, A. Riisager, ChemCatChem 2013, 5, 1754-1757. [18] a) R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba, M. López Granados, *Energy Environ. Sci.* 2016, *9*, 1144-1189; b) S. Srivastava, N. Solanki, P. Mohanty, K. A. Shah, J. K. Parikh, A. K. Dalai, *Catal. Lett.*
- 2015, 145, 816-823. [19] a) C. Wang, Z. Guo, Y.Yang, J. Chang, A. Borgna, Ind. Eng. Chem. Res. 2014, 53, 11284-11291; b) Å. O'Driscoll, J. J. Leahy, T. Curtin, *Catal. Today* 2017, 279, 194-201; c) Q. Yuan, D. Zhang, L. van Haandel, F. Ye, T. Xue, E. J. M. Hensen, Y. Guan, J. Mol. Catal. A: Chem. 2015, 406, 58-64
- [20] B. Tang, W. Dai, X. Sun, G. Wu, N. Guan, M. Hunger, L. Li, Green Chem. 2015, 17, 1744-1755.
- [21] J. Jae, W. Zheng, R. F. Lobo, D. G. Vlachos, ChemSusChem 2013, 6, 1158-1162
- [22] P. Panagiotopoulou, D. G. Vlachos, *Appl. Catal. A: Gen.* 2014, 480, 17-24
 [23] a) S. Huang, N. Yang, S. Wang, Y. Sun, Y. Zhu, *Nanoscale* 2016, 8, 14104-14108; b) X. Chen, L. Zhang, B. Zhang, X. Guo, X. Mu, *Sci. Rep.* 2016, 6, 28558; c) R. V. Sharma, U. Das, R. Sammynaiken, A. K. Dalai,
 Appl. Catal. A: Gen. 2013, *454*, 127-136; d) T. V. Kotbagi, H. R. Gurav, A. S. Nagpure, S. V. Chilukuri, M. G. Bakker, RSC Adv. 2016, 6, 67662-67668; e) M. Audemar, C. Ciotonea, K. D. O. Vigier, S. Royer, A. Ungureanu, B. Dragoi, E. Dumitriu, F. Jerome, *ChemSusChem* 2015, *8*, 1885-1891; f) J. Li, J. Liu, H. Zhou, Y. Fu, *ChemSusChem* 2016, *9*, 1339-1347
- [24] M. M. Antunes, S. Lima, P. Neves, A. L. Magalhães, E. Fazio, F. Neri, M. T. Pereira, A. F. Silva, C. M. Silva, S. M. Rocha, M. Pillinger, A. Urakawa, A. A. Valente, *Appl. Catal. B: Environ.* **2016**, *182*, 485-503.
- [25] A. J. Garcia-Olmo, A. Yepez, A. M. Balu, A. A. Romero, Y. Li, R. Luque, Catal. Sci. Technol. 2016, 6, 4705-4711.
- [26] a) R. Cohen, C. R. Graves, S. T. Nguyen, J. M. L. Martin, M. A. Ratner, J. Am. Chem. Soc. 2004, 126, 14796-14803; b) P. Nandi, Y. I. Matvieiev, V. I. Boyko, K. A. Durkin, V. I. Kalchenko, A. Katz, J. Catal. 2011, 284, 42-49 [27] X. Xiang, B. Zhang, G. Ding, J. Cui, H. Zheng, Y. Zhu, Catal. Commun.
- **2016**, *86*, 41-45. [28] a) M. Chia, J. A. Dumesic, *Chem. Commun.* **2011**, *47*, 12233-12235; b) S.
- J. Garibay, S. M. Cohen, Chem. Commun. 2010, 46, 7700-7702.

WILEY-VCH

FULL PAPER

Table of Contents

FULL PAPER

All from Biomass: Bio-based 2,5furandicarboxylic acid (FDCA) assembled with zirconium under solvothermal conditions can give mesoporous Zr-FDCA microspheres functionalized with enhancive Lewis acid-base centers, which are demonstrated to be highly active and selective for catalytic transfer hydrogenation and oxidation of biofuranics to corresponding alcohols and C4 products (see image), respectively. The robust and sustainable catalytic system shows great potential for efficient valorization of biofuranics.



H. Li, X. Liu, T. Yang, W. Zhao, S. Saravanamurugan, S. Yang*

Page No. – Page No.

Porous zirconium-furandicarboxylate microspheres for efficient redox conversion of biofuranics