Base-Free Aqueous-Phase Oxidation of 5-Hydroxymethylfurfural over Ruthenium Catalysts Supported on Covalent Triazine Frameworks

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The base-free aqueous-phase oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxilic acid (FDCA) was performed at 140 °C and 20 bar of synthetic air as the oxidant. Ru clusters supported on covalent triazine frameworks (CTFs) enabled superior conversion (99.9%) and FDCA yields in comparison to other support materials such as activated carbon and γ -Al₂O₃ after only 1 h. The properties of the CTFs such as pore volume, specific surface area, and polarity could be tuned by using dif-

Introduction

In the last decades, diminishing fossil resources have induced researchers to establish new routes for the production of fuels and chemicals. To become independent of depleting resources, a renewable feedstock such as biomass is a promising alternative.^[1] The major goal is to transform biomass-derived platform chemicals selectively to highly valuable chemicals, such as pharmaceuticals, polymer precursors, or fine chemicals.^[2] One such biomass-derived platform molecule is 5-hydroxymethylfurfural (HMF).^[3,4] This dehydration product of hexoses, such as glucose and fructose, has been transformed successfully into several valuable fine chemicals. HMF is discussed as one of the most versatile platform chemicals based on biomass.^[3] Interesting chemicals derived from HMF are its oxidation products 2,5diformylfuran (DFF) and 2,5-furandicarboxylic acid (FDCA),^[5] which are both considered as valuable precursors in the polymer industry (Scheme 1). DFF can be used as a precursor for furanic biopolymers, furan-urea resins, antifungal agents, and



Scheme 1. Oxidation pathway of HMF to FDCA over either HMFCA or DFF.

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ferent monomers. These material properties influence the catalytic activity of Ru/CTF significantly as mesoporous CTFs showed superior activity compared to microporous materials, whereas high polarities provide further beneficial effects. The recyclability of the prepared Ru/CTF catalysts was comparable to that of Ru/C at high conversions and product yields. Nevertheless, minor deactivation in five successive recycling experiments was observed.

pharmaceuticals.^[6–9] Moreover, FDCA has been identified by the U.S. Department of Energy as one of the top 12 valueadded chemicals based on biomass.^[10] A possible application of FDCA is the substitution of terephthalic acid in polyethylene terephthalate (PET) production.^[11] The company Avantium reported the superior properties of such completely biomass-derived polyethylene furanoate (PEF) materials.^[12] As another example, 2,5-bis(aminomethyl)tetrahydrofuran can be derived from FDCA and could be used in the production of new Nylon materials.^[10] Furthermore, FDCA can be converted directly to adipic acid.^[13]

The oxidation of HMF to FDCA has been performed with stoichiometric amounts of HNO₃, N₂O₄, and KMnO₄.^[14] As this technique is not feasible for large-scale applications, efforts have been made to use air or oxygen as an environmentally benign oxidant. Both homogenous (Co/Mn/Br)^[15] as well as a variety of heterogeneous catalysts have been used to synthesize FDCA from HMF, which include catalysts based on noble metals such as Pt, Pd, Au, and Ru.^[16,17] In particular, Au-based catalyst systems have gained attention as oxidation catalysts. Gupta et al. demonstrated the selective base-free oxidation to FDCA using a Au catalyst supported on hydrotalcite (Au/HT) at low temperatures of 95 °C and a flow of oxygen or air at ambient pressure.^[16c] After 7 h, FDCA yields of > 99% with pure oxygen and 81% with air at full HMF conversion could be obtained if a HMF/metal molar ratio of 40:1 was applied. Nevertheless, during recycling tests the yield decreased to 92% in the second run and 90% after the third cycle. Another interesting example was demonstrated by Wan et al. who used Au-Pd alloys on carbon nanotubes (CNT).^[16d] These catalysts enabled a yield of 94% FDCA at 0.5 MPa O_2 and 100 $^\circ$ C after 12 h. The HMF/metal ratio (100:1) was relatively high, and recycling studies revealed good stability with only minor deactivation in the first three cycles and stable FDCA yields up to the sixth run.



Nevertheless, as noble-metal catalysts based on Au, Pt, and Pd are rather expensive, Ru catalysts are economically attractive if we consider that the Ru price is ~4% of that of Au and Pt costs per gram.^[17] High yields of 95% of FDCA could be obtained using Ru(OH)_x supported on a hydrotalcite in water and DMF.^[18] Unfortunately, the Ru(OH)_x catalysts presented by Gorbanev et al. showed significant deactivation because of the leaching of the metal species and the decomposition of HT.

Recently, Nie et al. reported on Ru on various supports as efficient catalysts for the selective oxidation of HMF to DFF.^[19,20] They tuned the parameters and utilized water in the presence of a HT as a solid base to obtain 2,5-formylfurancarboxylic acid (FFCA) and FDCA in high yields of 83 and 78%.^[20] In a later study they investigated the influence of different solid bases as well as aqueous NaOH and concluded that HT leads to superior conversions and yields because of its appropriate basicity.^[21] Nevertheless, this approach still suffers from the significant leaching of Mg²⁺ ions from the HT support into solution caused by the formation of the acidic reaction products FFCA and FDCA.

Herein, we present the base-free catalytic oxidation of HMF to FDCA utilizing Ru catalysts stabilized on covalent triazine frameworks (CTF). CTF are a class of highly stable covalent organic frameworks formed by the polymerization of aromatic dinitriles in molten ZnCl₂.^[22] Thermally stable up to 400 °C and insoluble in most common solvents, acids and bases, these materials are suitable solid catalysts for use in sustainable chemistry.^[23] The selection of different dinitrile monomers enables the specific surface areas and pore volume of the porous CTF materials to be fine tuned. Furthermore, CTFs contain numerous nitrogen moieties that allow the coordination of different molecular catalysts before reduction. This enables both a molecular dispersion as well as stabilization of the metal species formed upon reduction on the solid support.^[24,25] Therefore, Ru/CTF materials become available that show high activity and selectivity in the aqueous-phase oxidation of HMF to FDCA and facilitate recycling because of the stabilization of the catalytically active species.

Results and Discussion

For synthesis of CTF materials with different structural properties such as specific surface area, total pore volume, and pore structure, 1,3-dicyanobenzene (1,3-DCB), 2,6-pyridinedicarbonitrile (2,6-DCP), 1,4-dicyanobenzene (1,4), and 4,4'-biphenyldicarbonitrile (4,4'-DCBP) were used as monomers (Scheme 2). Furthermore, the choice of monomer has significant influence on the N content of the resulting material.

All CTFs were synthesized in molten ZnCl₂, which serves as both solvent and Lewis acid catalyst during the reaction. A ZnCl₂/monomer molar ratio of 5:1 was chosen to obtain porous materials with exceptionally high specific surface areas.^[22] The monomer/salt mixture was heated sequentially for 10 h each at 400 and 600 °C, which led to the formation of a fully amorphous black solid with bimodal micro- and mesoporosity.

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Scheme 2. Monomers applied as linker in the CTF synthesis.

Admittedly, the N content of the formed CTFs is decreased in comparison to that of the applied monomer. An explanation is the increased temperature of 600 °C that favors partial carbonization of the material during synthesis. The N content, structural parameters, and the amount of Ru in the prepared catalysts are summarized in Table 1. The corresponding N₂

Table 1. Elemental analysis, specific surface area, total pore volume, andhydrophilicity of the CTF materials as well as Ru-content of the metal-loaded Ru/CTF catalysts.										
Monomer/	N ^[a]	$S_{BET}^{[b]}$	$V_{P(total)}^{[c]}$	$V_{P(H_2O)}^{[d]}$	DPF	Ru ^[e]				
material	[%]	[m ² g ⁻¹]	[cm ³ g ⁻¹]	[cm ³ g ⁻¹]	[%]	[%]				
CTF-a	9.5	2439	1.96	1.38	70.4	$(4.32)^{[f]}$				
CTF-b	17.2	1179	0.64	0.56	87.5	$(3.34)^{[f]}$				
CTF-c	10.4	2071	1.36	0.99	72.8	$(3.91)^{[f]}$				
CTF-d	3.7	1683	2.63	0.75	28.5	$(3.99)^{[f]}$				
Ru/C	-	720	0.70	0.35	50.0	$5.00^{[g]}$				
Ru/CTF-a	9.5	2152	1.59	1.35	84.9	4.32				
[a] Determined by elemental analysis. [b] Surface area identified by the BET method. [c] Total pore volume determined at $p/p_0 = 0.98$. [d] Water uptake determined by H ₂ O vapor physisorption at $p/p_0 = 0.90$. [e] Determined by ICP-OES after immobilization and reduction of RuCl ₃ ·xH ₂ O under H ₂ for 3 h at 350 °C. [f] Metal loading refers to the final catalyst materials, whereas the structural parameters relate to the support before Ru loading; [g] Data provided by Sigma–Aldrich.										

physisorption isotherms and pore size distributions calculated by a N_2 -DFT model are given in Figure S1. The effect of the monomer on the resulting structure is illustrated in Scheme S1.

As the oxidation of HMF to FDCA with Ru-based catalysts is achieved in aqueous reaction media, H_2O vapor physisorption measurements were conducted to obtain knowledge about the hydrophilicity of the CTF materials studied in this work. The H_2O vapor physisorption isotherms for all materials studied in this work are illustrated in Figure 1.

The H_2O vapor physisorption isotherms indicate strong water uptake for most CTF materials presented in this work, which correlates to a superior hydrophilicity and polarity than Ru/C (Figure 1). CTF polymers based on 1,3-DCB (CTF-a) show the highest total amount of water adsorbed, followed by CTF materials based on 1,4-DCB (CTF-c) and 4,4'-DCBP (CTF-d).

The lowest uptake of water occurs for a microporous CTF material based on 2,6-DCP (CTF-b), which is still higher than that of Ru/C. To obtain insights into the polarity and, therefore,



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Figure 1. H₂O vapor physisorption isotherms of different CTF materials based on various linker molecules as well as Ru/C (×: adsorption, \odot : desorption) measured at 19.5 °C.

the hydrophilicity of the material, the degree of pore filling (DPF) was calculated. This value reflects the uptake of water over the total pore volume. For N-rich CTF-b, the DPF is highest at 87.5%, followed by CTF-c and CTF-a because of their structural similarities (72.8 and 70.4%). The low N content of CTF-d results in a strong hydrophobicity compared to all other materials highlighted by a very low DPF of 28.5%. Furthermore, a pronounced desorption takes place at a relative pressure of 0.36 for CTF-a and CTF-c, which is most probably related to the bimodal micro- and mesoporosity of these materials. For microporous CTF-b, a minor desorption step at a low relative pressure occurs. An explanation might be the stronger interaction of water molecules with the high amount of nitrogen functionalities, which delays desorption in comparison to that of CTF-a and CTF-c with lower N contents. CTF-d lacks this phenomenon because of its mesoporous nature and low N content. For Ru/CTF-a compared to CTF-a, a similar water sorption isotherm could be observed together with an identical total amount of adsorbed water at a relative pressure of 0.9 and only minor changes of the DPF (70.4 vs. 84.9%; Table 1), which can be assigned to the lower total pore volume of the metal-loaded material. In contrast, Ru/C exhibits a low water uptake and a DPF of only 50.0%.

In a stepwise coordination and reduction protocol, for all CTF materials a final metal content of 3.3–4.3 wt% Ru could be achieved (Table 1 and Scheme 3). Both SEM with energy-dispersive X-ray spectroscopy (EDX) mapping and TEM confirm metal species distributed finely throughout the whole solid support after reduction as discussed in a previous study.^[26] Even if reduced under a H₂ atmosphere at 350 °C, no metal nanoparticles or agglomerates are observed by TEM. Furthermore, the powder XRD patterns of the catalysts show no reflections of Ru⁰ metal species formed after reduction of the coordinated complexes. Accordingly, the Ru nanoparticles formed under these conditions are rather small and, therefore, X-ray amorphous. We assign these observations not only to an efficient pre-coordination but also to a stabilization effect provided by the N moieties of the CTF materials.^[25,26]



Scheme 3. a) Synthesis of a CTF based on 1,3-DCB as a monomer (CTF-a). b) Coordination of RuCl₃·x H₂O to form immobilized Ru@CTF-a. c) Proposed stabilized metal nanoparticles after reduction in the presence of pure H₂.

Catalytic oxidation of HMF to FDCA

Recently, we showed that Ru/CTF catalysts are promising materials for the oxidation of HMF to DFF using methyl tert-butyl ether as the solvent and air as the sole oxidant under mild conditions.^[26] In this study we observed that HMF is overoxidized to FFCA in the presence of water. Nevertheless, the parameters chosen for the selective oxidation of HMF to DFF were relatively mild, and even in water, only trace amounts of FFCA were formed. Nie et al. demonstrated a similar effect for Ru/C. In the presence of water and at high temperatures of up to 150 °C, the selectivity could be shifted towards FDCA formation.^[20] The addition of a HT as solid base even increased the FDCA yield. Experiments conducted with ¹⁸O₂ revealed water as the source of oxygen for the oxidation of the formyl group as already discussed for HMF oxidation over Pt and Au catalysts.^[27] For comparison with the system presented by Nie et al., knowledge of the exact reaction times utilized in their study would be necessary, which are not provided in the publication. Still, we also observe that FDCA is formed by the oxidation of HMF to DFF and consecutive oxidation to FFCA at higher temperatures. No 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) was observed if supported Ru was used as the catalyst.

To see how the Ru/CTF catalysts perform in the oxidation of HMF to FDCA in aqueous media compared to Ru/C, the performance of commercially available Ru/C was studied first. The influence of temperature, air pressure, and reaction time was investigated. At an initial pressure of 20 bar of synthetic air, close to full conversion could be achieved after 1 h at 120 °C, and the main products formed are DFF (38.3%) and FFCA (45.6%). An increase of the temperature to 140 °C led to an increase of the FFCA (53.2%) and FDCA yields (23.7%). A further increase of the air pressure at 140 °C led to higher FDCA yields of up to 37.5% at 40 bar. Nevertheless, only minor changes of the FDCA yield occur at pressures above 30 bar of synthetic air (Figure 2).

During the heating of the autoclave to the desired temperature of 140 $^\circ C$ (≈ 25 min), a certain conversion already occurs





Figure 2. Catalytic conversion (X) and yield (Y) with the variation of a) temperature and b) the initial pressure of air. Only one parameter was changed at a time. Reaction conditions: 1 h, 140 °C, 20 bar of air, 15 mL water, 500 rpm stirring speed, Ru/C, HMF/metal molar ratio 40:1.

(Figure 3, 0 h). A prolonged reaction time of 3 h led to FFCA and FDCA yields of up to 11.2 and 69.9%. Unfortunately, the C balances were not entirely closed, and prolonged reaction times of up to 5 h led to even worse results. In previous studies, we showed that the adsorption of HMF and its oxidation products on the surface of different solid supports is favored.^[26,28] Additionally, this effect might be attributed to the low solubility of FDCA in water, which will further increase the adsorption probability.



Figure 3. Time-resolved conversion (*X*) and yield (*Y*) over Ru/C. Reaction conditions: $140 \degree$ C, 20 bar of air, 15 mL water, 500 rpm stirring speed, HMF/ metal molar ratio 40:1. Y(FDCA)* and C-Balance* were obtained on washing the catalyst with 80 mL of DMSO after catalysis.

Adsorption measurements performed with FDCA as the adsorbate from aqueous solutions confirmed the adsorption effect for both Ru/C and Ru/CTF-a. Amounts of adsorbed FDCA (based on the initial amount of FDCA) as high as 13.3% for Ru/ C and 11.3% for Ru/CTF-a were observed utilizing a model system composed of water and the maximum amount of FDCA formed for 100% yield. Therefore, we assume that the adsorption of HMF as well as DFF, FFCA, and FDCA takes place under these reaction conditions. Still, traces of oligomeric byproducts could be formed, which would not be detected by HPLC but would contribute to the gap in the carbon balance.^[29]

The influence of different support materials has been studied at 140 °C and 20 bar of air after 1 h reaction time, which allows the full conversion of HMF and moderate selectivity towards FDCA for commercial Ru/C (Table 2). In the absence of a catalyst, 62.9% of HMF was converted with furfural and polymeric species as the major products, which results in an orange solution with a brownish precipitate that smells intensely of caramel.

Initially, Ru/C was calcined for 4 h at 300 °C under an air flow to form Ru_{ox}/C. This catalyst achieved only 80.1 % HMF conversion and allowed a significantly lower yield of FDCA (8.6%) compared to Ru⁰/C (23.7%) under the same conditions (Table 2, entry 2 vs. 3). Therefore, we assume that Ru⁰ is the catalytic active species as Ru_{ox} appears to be less active.

 Ru/γ -Al₂O₃ and Pd/C exhibited only low conversions and did not yield FDCA at all (Table 2, entries 4 and 5). In contrast, Pt/C appears to be very active and yielded 56.3% FDCA at full conversion after 1 h. Nevertheless, the C balance was only 66.8%. Strong adsorption on the catalyst surface and the formation of polymeric byproducts or oligomeric compounds of FDCA and

Table 2. Catalytic activity with the variation of the support material andoxidation state of Ru. Reaction conditions: 1 h, 140 °C, 20 bar of air,15 mL water, 500 rpm stirring speed, HMF/metal molar ratio 40:1.

Entry	Catalyst	X [%]	Y(DFF) [%]	Y(FFCA) [%]	Y(FDCA) [%]	C balance [%]
1	_[a]	62.9	3.3	0.0	0.0	59.6
2	Ru _{ox} /C	80.1	25.3	33.2	8.6	88.4
3	Ru/C	99.9	13.5	53.2	23.7	91.1
4	$Ru/\gamma-AI_2O_3$	32.4	19.3	4.4	0.0	93.4
5	Pd/C	35.1	12.5	2.1	0.0	84.3
6	Pt/C	100	0.0	10.5	56.3	66.8
7	CTF-a	19.9	2.7	0.0	0.0	83.1
8	Ru/CTF-a	99.9	9.9	35.3	37.7	83.7
9	Ru/CTF-b	93.7	35.8	24.2	8.2	75.2
10	Ru/CTF-c	99.9	7.5	34.8	41.4	84.3
11	Ru/CTF-d	100	10.2	46.0	33.4	90.1
12	Ru/C ^[b]	96.5	17.0	55.2	20.4	96.7
13	Ru/C ^[b,c]	100	1.6	35.8	47.8	86.0
14	Ru/C ^[b,d]	100	0.2	23.7	62.8	87.6
15	Pt/C ^[b]	100	0.0	14.6	64.7	79.3
16	Ru/CTF-c ^[b]	99.3	8.8	39.6	43.6	93.4
17	Ru/CTF-c ^[b,d]	100.0	0.1	10.6	77.6	89.1

Conversion (X), yields (Y), and C balance determined by HPLC. Traces of furfural (<1.0%) and furoic acid (<0.5%) were formed as byproducts in all experiments. [a] 19.1% Furfural was formed. [b] washed with DMSO (80 mL) [c] Prolonged reaction time of 2 h. [d] 3 h reaction time.

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its byproducts can be assumed. Particularly with regard to metal prices, Ru is a very attractive alternative.

Ru catalysts supported on CTF polymers showed the highest activity and productivity compared to Ru/C and Ru/ γ -Al₂O₃. The activity of various Ru catalysts on CTF supports based on different material precursors (Scheme 3) has been studied. The use of only the CTF-a support resulted in a low HMF conversion of 19.9%. Interestingly, only trace amounts of furfural (< 0.1%) were formed and the solution did not change color, which highlights the absence of polymeric byproducts and the facile adsorption of HMF as the major origin of the gap in the C balance.

Mesoporous Ru-doped CTF materials with high specific surface areas showed a high selectivity towards FDCA (up to 41.4% after 1 h; Table 2, entry 8-11) at full conversion. An increase of the reaction time did result in higher FDCA yields (up to 53.3% for Ru/CTF-a), but the C balance decreased to 61.1% because of the low solubility of FDCA, product adsorption, and the potential formation of polymeric or oligomeric byproducts with water as the solvent. For microporous CTF-b, which has a significantly lower specific surface area and pore volume, a decrease in both the conversion and FDCA yield occurred (93.7 and 8.2%; Table 2, entry 9). Therefore, it seems that HMF conversion and FDCA yield can be correlated mostly to the porosity and water uptake of the various CTF materials. Consequently, mesoporosity is more advantageous for high catalytic activity than pure microporosity. Interestingly, the highest FDCA yield was achieved with CTF-c as the support material even though it exhibits only modest porosity compared to the other mesoporous materials, CTF-a and CTF-d. In this case, high polarity related to hydrophilicity seems to provide a beneficial effect (Table 1). Within the mesoporous CTF materials, the DPF of CTF-c is the highest followed by that of CTF-a and CTFd, and the latter is mostly hydrophobic. In line with these findings, the highest FDCA yield was found for CTF-c, followed by CTF-a and CTF-d. Therefore, the porosity, specific surface area, and hydrophilicity of the solid support influence the catalytic performance significantly.

The influence of the adsorbed surface species on the loss in the C balance because of their low solubility in water was examined for the most active Ru/C, Pt/C, and Ru/CTF-c catalysts. Therefore, the catalysts were washed extensively with 80 mL DMSO after reaction (Table 2, entries 12-17). For all catalysts, the gap in the mass balance became significantly smaller as the amount of adsorbed acid species makes a contribution to the product yields. At prolonged reaction times of up to 3 h, the C balance decreases slightly, which might be attributed to the formation of polymeric byproducts formed upon FDCA production (Table 2, entries 12-14 and 16-17). For Pt/C, the C balance under the same conditions is at least 10% smaller. This can be explained by stronger acid-metal interactions as discussed previously.^[30] Ru/CTF-c yields twice the amount of FDCA after 1 h and approximately 15% more of the desired product after 3 h compared to Ru/C under the same reaction conditions.

Notably, DFF, FFCA, and FDCA were the major products observed for all the studied catalysts. Nevertheless, under these conditions, traces of furfural were present, which was further oxidized to furoic acid. Most C balances are not closed. Again, as no side-products are formed, we assume the adsorption of HMF, DFF, FFCA, and FDCA on the solid support materials. Furthermore, the formation and adsorption of polymeric byproducts on the catalyst surface cannot be excluded at this point.

To compare the catalytic long-term stability, the most active Ru/CTF-c catalyst and Ru/C have been recycled in five successive runs (Figure 4).



Figure 4. Conversion (*X*) and yield (*Y*) during the recycling study of a) Ru/C and b) Ru/CTF-c. Reaction conditions: 1 h, $140 \,^{\circ}$ C, 20 bar of air, 15 mL water, 500 rpm stirring speed; HMF/metal molar ratio 40:1.

For both catalysts, activity was lost if the material was simply washed with an organic solvent and dried in vacuum, and further treatments to regain activity were necessary. These findings imply that not only polymeric species are formed on the catalysts surface but the surface oxidation of the metal nanoparticles also takes place, which causes the observed loss in activity. Therefore, the catalysts were washed thoroughly with acetone and reactivated at 350 °C for 3 h under H₂ flow. This approach reduced the deactivation significantly (Figure 4).

Both catalysts show good recyclability. Ru/C and Ru/CTF-c exhibit only minor deactivation over five successive catalyst cycles. Furthermore, Ru/CTF-c can maintain its superior activity compared to Ru/C up to the fourth cycle with 36.6% FDCA yield compared to that of 21.0% for Ru/C, respectively.

Nevertheless, the yield of FDCA decreases more drastically in the fifth cycle for Ru/CTF-c. Certainly deactivation by adsorption and the formation of polymeric species play a crucial role. Additionally, the experimental error increases because of the distinct loss of catalyst upon recycling as 50 mg Ru/CTF-c was



used for the first cycle and below 15 mg was used for the fifth cycle. The overall high yield in all five cycles leads to higher amounts of adsorbed species, which makes subsequent polymerization of FDCA more likely in the case of Ru/CTF-c and leads to faster deactivation.

As mentioned in our previous studies, physisorption indicates the formation of polymeric byproducts on the catalyst surface, which are not removed by simple washing. However, the rather harsh reduction conditions applied in our studies seem to be reliable to accomplish the decomposition of adsorbed polymeric species and, therefore, facilitate catalyst reactivation. It can be assumed that both the surface species and oxidation of the metallic species are the most probable reasons for deactivation and the leaching of the active species plays a minor role. This could also be confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES) of the aqueous solution after catalysis as well as a hot-filtration test (Table S1). In this test the filtrate after the removal of the catalyst was allowed to react for 1 h at 140 $^\circ$ C and 20 bar. This did not result in the further conversion of HMF, although the FFCA and FDCA yields increased slightly (1.4 and 0.1%, respectively), which is likely to occur in the absence of catalyst. Nevertheless, under these reduction conditions, agglomeration and the loss of the external metal surface area cannot be excluded. Future studies will focus on a more comprehensive understanding of deactivation mechanisms that occur during the oxidation of HMF over supported Ru catalysts. The discussed correlation of activity, porosity, and surface polarity offers the first insights with regard to the importance of tailored interactions between the solvent, substrate, and catalyst surface.

Conclusions

We have presented a new catalyst system based on Ru supported on covalent triazine frameworks (CTF) that catalyzes the base-free oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxilic acid in water efficiently. Bimodal micro- and mesoporous CTF supports with large specific surface areas were accessible and contained variable amounts of N moieties. The control of the structural parameters of the CTF tunes the catalytic activity as microporous materials show only low activities compared to mesoporous CTFs. The specific surface areas of the materials play an important role during catalysis, and the N content seems to influence the polarity of the material significantly as indicated by H₂O physisorption. The polarity of the materials provided a further beneficial effect during catalysis performed in water. High conversions and yields of furandicarboxylic acid could be obtained at 140°C and 20 bar initial air pressure. Both Ru/C and Ru/CTF-c showed promising recyclability. Nevertheless, to obtain satisfactory C balances, washing with DMSO was inevitable. Reactivation of the catalyst is challenging, and rather harsh conditions (350 °C, H₂ flow) need to be applied to maintain the catalyst activity. However, only batch reactions have been performed so far, and continuous reactions will be conducted in future studies. Furthermore, the oxidation could be performed with air as the most abundant and sustainable oxygen resource over a catalyst based on Ru

as a relatively cheap noble metal in the absence of a base. This procedure facilitates product separation and enables environmentally benign processing.

Experimental Section

Preparation of the catalysts

For the synthesis of CTF-a, 1,3-dicyanobenzene (0.621 g, 4.85 mmol, 1 equiv.) and ZnCl₂ (3.305 g, 24.25 mmol, 5 equiv.) were mixed and ground together, transferred into a guartz ampoule, and dried in vacuum for at least 3 h. The ampoule was then flamesealed and placed inside a furnace for 10 h at 400 °C and 10 h at 600 °C (heating rate: 10 °C min⁻¹). After cooling to RT, the ampoule was broken open (CAUTION: the ampoules are under pressure, which is released during opening), and the solid product was ground and washed with water and diluted HCl (0.1 M) thoroughly. The solid material was then ground by using a ball mill (Fritsch Pulverisette23, 5 min, 30 Hz) to obtain a black powder, which was washed successively with water, diluted HCl, diluted NaOH, water, and THF, and was dried under vacuum for at least 12 h. Materials based on 2,6-pyridinedicarbonitrile (CTF-b), 1,4-dicyanobenzene (CTF-c), and 4,4'-biphenyldicarbonitrile (CTF-d) were synthesized in the same way. For Ru impregnation, CTF (600 mg) was added to a solution of RuCl₃·xH₂O (0.079 g, 0.381 mmol) in EtOH (400 mL) heated to reflux and stirred for 6 h. After cooling to RT, the Ru^{III}@CTF material was then collected by filtration and washed with EtOH to remove any uncoordinated Ru precursor. After drying under vacuum at 60 °C for at least 12 h, the Ru^{III}@CTF material was reduced under H₂ by using a tube furnace (heating rate: 10° C min⁻¹, 350°C, H₂ flow 100 mL min⁻¹, 3 h) to obtain Ru/CTF (for Ru loading see Table 1). Ru/C, Ru/ γ -Al₂O₃, Pd/C, and Pt/C catalysts (5 wt%) were purchased from Sigma-Aldrich and were used as received. The CTF materials were characterized by thermogravimetric analysis, elemental analysis, N_2 and H_2O vapor sorption measurements, TEM, and XRD. N₂ physisorption measurements were conducted by using a Micromeretics ASAP 2010 measurement device at -195.8°C by a static volumetric method. H₂O vapor sorption measurements were performed by using an Autosorb iQ₂ measurement device at 19.5 °C by a static volumetric method. For both sorption measurements samples were activated at 250 °C by using a FloVacDegasser for at least 15 h. The DPF was calculated as follows [Eq. (1)]:

$$\mathsf{DPF} = \frac{V_{\mathsf{P}(\mathsf{H}_2\mathsf{O})}}{V_{\mathsf{P}(\mathsf{total})}} \times 100\% \tag{1}$$

with $V_{P(H_2O)}$ being the water uptake determined by H₂O vapor physisorption at $p/p_0 = 0.90$ and $V_{P(total)}$ being the total pore volume determined at $p/p_0 = 0.98$.

The Ru-doped materials were analyzed by ICP-OES, SEM-EDX, TEM, and XRD.

Selective oxidation of HMF to FDCA

Typically, a stainless-steel autoclave (75 mL) with a glass inlet was charged with a solution of HMF (0.1261 g, 1 mmol) in H_2O (15 mL). The catalyst (0.05 g for Ru- and Pd-based catalysts, 0.10 g for Pt/C, HMF/metal molar ratio: 40:1) was added, and the autoclave was equipped with a stirring bar and temperature sensor. It was sealed, pressurized to 20 bar with synthetic air (hydrocarbon free), and heated to 140 °C with stirring at 500 rpm. After a certain time, the autoclave was cooled and depressurized. The reaction mixture was



diluted in water in a volumetric flask to enable the complete dissolution of FDCA. The catalyst was removed by filtration with a syringe filter (CHROMAFIL Xtra, PA-20/25, 0.20 µm), and the reaction solution was analyzed by HPLC (Shimadzu 2020, 300×8.0 mm organic acid resin column, T=40 °C, UV detector at $\lambda=254$ nm for HMF and DFF, RID-10 A detector for HMFCA, FFCA, and FDCA) with trifluoroacetic acid (154 µL) in water (1 L) as the eluent (flow rate: 1 mLmin⁻¹). For recycling studies, the catalysts were collected by filtration by using a Whatman filtration system equipped with Anodisc 25 (0.20 µm) membranes, washed thoroughly with solvent, dried overnight under vacuum at 60 °C, and reactivated under H₂ by using a tube furnace (10 °Cmin⁻¹, 350 °C, H₂ flow 100 mLmin⁻¹, 3 h) to regain activity.

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Keywords: biomass · oxidation · heterogeneous catalysis · ruthenium · supported catalysts

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