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FULL PAPER

Leather promoted transformation of glucose into 5-hydroxymethylfurfural and levoglucosenone.

Felix D. Bobbink, Zhangjun Huang, Florent Menoud, Paul J. Dyson*

Abstract: The search for efficient catalysts frequently leads to new homogeneous and heterogeneous catalysts of increasing complexity, sometimes overlooking common, natural or hybrid natural-synthetic materials that could be used in catalysis. For example, the leather industry has produced very robust materials for centuries, via the chemical treatment of animal hides with chromium salts and other chemicals, leading to robust Cr-containing materials. We report here the use of chromium-tanned leather as a heterogeneous catalyst for glucose dehydration into 5-hydroxymethylfurfural (5-HMF) and levoglucosenone (LGO). We applied a range of characterization techniques including FT-IR, SEM, BET, XRD and XPS on four waste leather pieces from shoe soles and a belt, and evaluated their catalytic activity. The activity of the scrap leather pieces compare favorably to many recently reported catalysts for the preparation of 5-HMF, but additionally results in significant quantities of LGO. Overall, our results demonstrate that waste leather is an outstanding material for use in catalysis.

Introduction

The transformation of lignocellulosic compounds into key platform chemicals has attracted considerable attention in recent years.[1–4] In particular, the transformation of cellulose and glucose into 5-hydroxymethylfurfural (5-HMF) has been extensively investigated because of the low cost and availability of the starting materials combined with the versatility of the product (see Figure 1).[5] In this context, a plethora of metal-based and non-metallic catalysts have been reported (See Table S1 for examples) to generate 5-HMF.[6–14] Other valuable products that can be derived from biomass sources include levoglucosenone, furfural, levulinic acid, etc.[15–17] The catalytic tools developed aim to be cheap and efficient, and it has been shown that ionic liquids (ILs) in combination with chromium salts (especially halide salts) efficiently catalyze the transformation of glucose into 5-HMF.[18,19] Several examples of heterogeneous chromium catalysts in combination with ILs have also been developed and evaluated for the reaction.[20–22] Inspired by these reports, we have identified chromium-tanned leather as a potential cheap and available catalyst for the reaction. Furthermore, the pH of leather is typically low, i.e. acidic, because of the treatment required during the tanning process, which is advantageous for the transformation since acid catalysts have been described.[23,24]

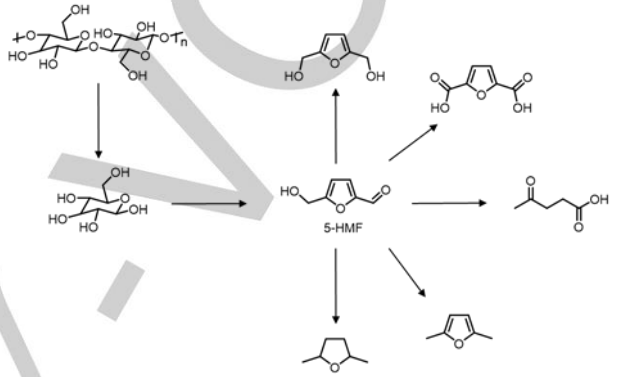

Figure 1. Transformation of cellulose (via glucose) to the platform chemical 5-HMF and examples of chemicals that can be derived from 5-HMF.[25–28]

The high Cr content leads to challenges in terms of waste treatment, and heavy pollution is associated with the treatment of tanned leather scraps and tanning baths. Hence, finding alternative uses of waste chromium-containing leather is of interest.[29–35] In this respect, some processes have recently been developed to recycle leather and use it in different applications (for example in pigments).[36,37] With respect to catalysis, chromium tanned leather can be regarded as a heterogeneous chromium-based catalyst embedded into an organic support composed of collagen and other skin components (proteins, amino acids, see Figure 2 for a tentative structure of the Cr complex formed with leather. Other type of cross-linking Cr species may be present simultaneously). Consequently, we decided to evaluate waste leather pieces as catalysts for the transformation of glucose into 5-HMF in various solvents. The leather pieces were characterized by a range of techniques including ICP-OES, SEM, XRD, FT-IR and XPS. Leaching tests were performed to assess the dynamic bound-release balance between the chromium and the collagen support during reaction, which is important since chromium is allergenic (even in its +3 oxidation state) and Cr(VI) compounds are carcinogenic.[38,39] Notably, reports describing the use of Cr(II) or Cr(III) salts do not mention the waste processing issues, in contrast to reports on Cr-tanned leather waste treatment, where many reports describe the risk of Cr(VI) contamination during waste treatment (e.g. during pyrolysis).[40]

[a] Felix D. Bobbink, Zhangjun Huang, Florent Menoud, Paul J. Dyson*
EPFL SB ISIC LCOM
Ecole polytechnique Fédérale de Lausanne (EPFL)
Avenue Forel, 1015 Lausanne
E-mail: pjd@epfl.ch

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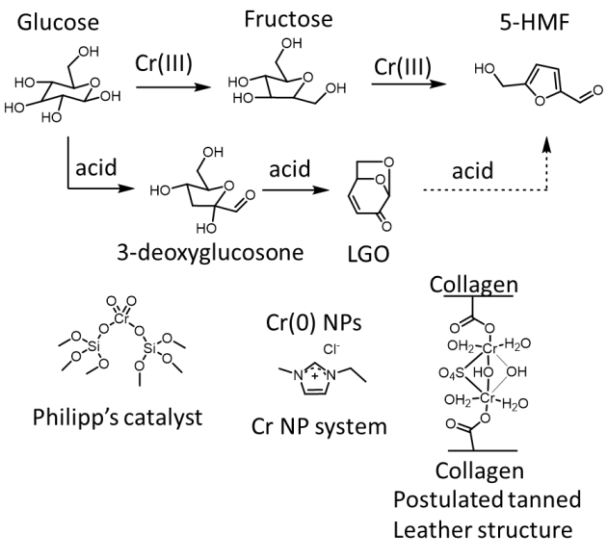

Figure 2. Proposed pathways for the transformation of D-glucose into 5-HMF (top) and selected Cr-based catalysts (bottom) left: Cr catalyst used for ethylene polymerization, middle: Cr(0) NPs used for glucose dehydration, right: proposed structure of Cr-tanned leather.[7,21,41]

Results and Discussion

Characterization of the leather catalysts

The pieces of scrap leather originated from shoe soles (**1-3**) and a belt (**4**). For analysis and utilization as catalysts, the leather was cut into small pieces (ca. 16 – 36 mm^2, see Figure 3 for representative examples). The pieces were not ground into shreds but were kept as a solid piece, to ensure facile processing and recycling (as the leather may be considered as a Cr catalyst immobilized on a structured material comparable to carbon fibers).[42]

ICP-OES analysis was performed on the leather pieces to quantify the Cr content, see Table 1, with the total content of Cr in the samples ranging from 7.84 µg/mg (lowest, **4**) to 18.13 µg/mg (highest, **1**). According to literature, the Cr content can contribute to up to 5 wt% of the total mass of leather.[43] The values obtained here are inferior to 5 wt% and correspond to approximately 1 wt% of Cr. Table S7 displays other elements that were present in **1** (determined by ICP-OES), with the main metals comprising Fe, Al, Mg, and Ti, Mn, Ni, albeit at concentrations 100 to 10 000 times lower than Cr. A simple colorimetric test using diphenylcarbazide was performed to estimate whether Cr(VI) was present in the leather pieces.[44] The test indicated that **2** contained Cr(VI). The pH of **1-4** was measured according to a modified ISO 4045:2008 procedure. Briefly, a piece of leather (approx. 20 mg) was extracted in deionized water (2 mL) for 6 h and the pH of the aqueous phase was measured. The pH of **1-4** ranges between 4.0 and 4.6, which is in the expected range for leather. XPS analysis confirmed the presence of Cr in all four samples but it was not possible to unambiguously determine the oxidation state of the Cr (Figures S7-S10 in the SI).[44] Samples **1-4** give three main peaks, i.e. corresponding to C1s, O1s and N1s, in the ranges 280-291, 526-536 and 395-404 eV, respectively, which is expected since leather is composed mainly of amino acids and other skin components. **1-3** also display peaks between 575 and 580 eV, whereas no further peaks were apparent in **4**. These high binding energies are associated with either hexavalent chromium species or chromium sulfate species, with the latter being more likely in leather samples because Cr(VI) species are banned from leather samples and would typically be reduced to Cr(III) species by components naturally present in leather. The Cr to S content (probe of the utilization of $Cr(SO_4)OH$ as tannin, defined as Cr/(Cr+S)) is 41% for **1**, 59% for **2**, 40% for **3** and 36% for **4**, with the ideal value being 50% and differences from the theoretic value being associated with the quality of the tanning agent used.[45] FT-IR spectroscopy was performed on both sides (smooth or fibrous) of the leather pieces and revealed that the spectra depends on the side of the leather analyzed. All samples contained typical collagen-type peaks (see Figure 3 and Figure S6) that match those of literature.[46,47] In particular, the peaks at 2928 and 2857 cm^{-1} are attributed to C-H stretches of fatty acids, presumably derived from the treatments.[44] The peaks at 1645, 1545 and 1275 cm^{-1} may be attributed to the amino acids (C=O stretch, N-H bend, C-N stretch, respectively).[46]

Table 1. Main characteristics of the leather samples.

Sample	1	2	3	4
Cr [µg/mg]	18.13	17.07	9.41	7.84
Surface area [m^2/g]	14.8	4.4	6.5	14
pH*	4.6	4.0	4.3	4.5

* determined according to the ISO 4045:2008 standard procedure for leather acidity measurement based on the pH of an aqueous extraction phase of the leather.

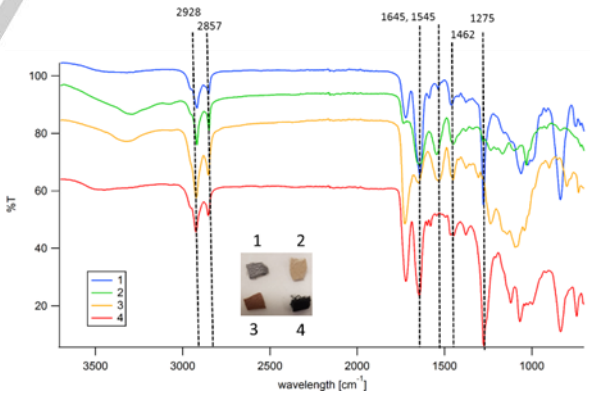

Figure 3. FT-IR spectra of the smooth side of the leather samples.

The SEM images of **1-4** (see Figure 4) show that all four leather samples are composed of a flat surface with a fibrous inner structure. The smooth face appears to be non-porous and the Cr content on the smooth face is very low compared to the Cr content contained in the fibrous structure according to the EDS analysis (Tables S2-S5, Figures S1-S4). BET analysis revealed a surface area of 14.8 m^2/g for **1**, 4.4 m^2/g for **2**, 6.5 m^2/g for **3** and 14 m^2/g

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for **4** (Table 1). These small surface areas are comparable to previous BET measurements of leather.[48]

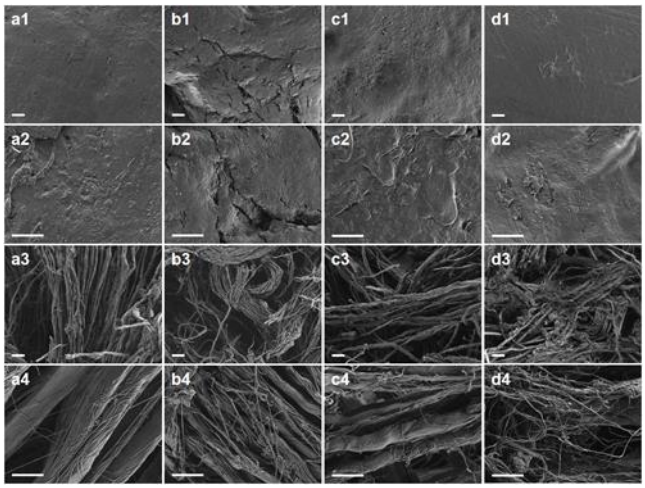

Figure 4. SEM images of the four leather samples (one column for each sample, **1-4** from the left). Rows 1 and 2 correspond to images of the smooth leather surface, rows 3 and 4 correspond to images of the fibrous surface. Rows 2 and 4 are magnified images of rows 1 and 3, respectively. The short and long scale bars are 20 µm and 5 µm, respectively.

The leather samples display some crystallinity on the smooth side, but no diffraction peaks were observed on the fibrous side (see Figure 5 for the XRD patterns of **1-4**, smooth side facing the detector) and it would appear that Cr_2O_3-type structures are present in **3**. Samples **1** and **3** suggests that a tetragonal phase is present with high yield (with the prototype $TiO_2/TiCrO_2$, see Figures S11-12 for Rietveld refinement). Note, the concentration of Ti in **1** is very low compared to Cr, and hence the catalytic activity (see below) is considered to be primarily due to the Cr, despite other metals potentially playing a role. Sample **4** displays the lowest crystallinity. The varying degree of crystallinity throughout the sample series is expected since tanneries employ different chemicals (TiO_2, for example), conditions and hides.

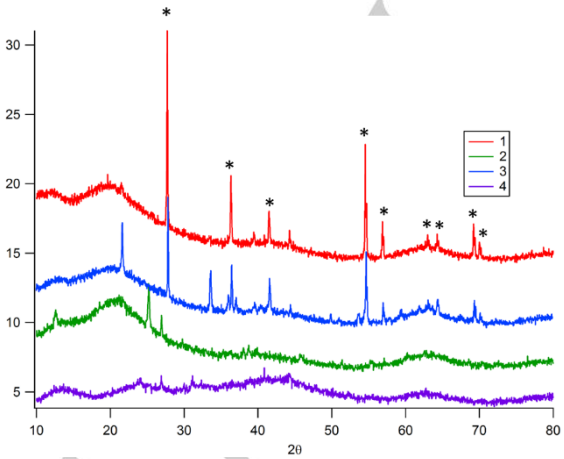

Figure 5. XRD spectra of leather pieces **1-4** (smooth surface facing the detector). *= $TiCrO_2$

Catalytic evaluation of the leather

The leather pieces (**1-4**) were evaluated in the dehydration of D-glucose to 5-HMF, since a range of Cr salts are excellent catalysts for this reaction.[20–22] Chromium halide salts are the most extensively studied catalysts for this reaction, although chromium oxides have been employed.[22]

We began our investigation by evaluating **1** in DMSO-d6 at different temperatures, in combination with a glucose concentration of 50 mg/mL. It should be noted that 5-HMF, due to its instability, requires careful tuning of the reaction parameters and/or a continuous extraction process to ensure high yields. The instability of 5-HMF and the possibility of forming humins and other side products often leads to modest yields, typically ranging from 20 – 70%.[49–56] Here, the yield of 5-HMF was determined by ^{1}H NMR spectroscopy using CH_2Br_2 as internal standard, and the identity of the product was further confirmed by GC-MS (see Experimental and Figures S6-S9 for representative ^{1}H NMR spectra). At temperatures below 165 °C, no reaction was observed with 5-HMF only starting to form at 165 °C (Table 2, entries 1-3). This reaction temperature is ca. 40% higher than that used in recent reports. In the absence of catalyst, at 165 °C no 5-HMF was observed (Table 2, entry 4). Note, DMSO is an excellent solvent for glucose conversion because of the high glucose solubility, however, DMSO is not active on its own because it does not promote glucose isomerization to fructose, although DMSO promotes the transformation of fructose into 5-HMF.[57] Under catalyst-free conditions, D-glucose anomerized at 165 °C (see NMR spectrum in Figure S6). When D-fructose was used as a substrate, the yield of 5-HMF was essentially the same when either **1** or no catalyst was employed (72% and 69%, respectively, reaction conditions: 50 mg D-fructose, 165 °C, 4 h), indicating that the catalyst, despite being acidic (pH ranging from 4 to 4.6, see Table 1), does not promote the conversion of fructose to 5-HMF. Instead, the catalyst promotes the isomerization of glucose into fructose, as has been previously shown in the case of Cr-catalyzed reaction.[18,58]

Table 2. Optimization of the reaction conditions.

Entry	Cat. (wt% Cr)	Solvent	T [°C]	Time [h]	Yield 5-HMF [%]	Yield LGO [%]
1	**1** (0.75)	DMSO-d6	135	0.5	0	0
2	**1** (0.75)	DMSO-d6	150	0.5	0	0
3	**1** (0.75)	DMSO-d6	165	0.5	20	0
4	-	DMSO-d6	165	0.5	0	0
5	**1** (0.36)*	DMSO-d6	165	1.5	7.5	6.2
6	**2** (0.34)*	DMSO-d6	165	1.5	12	4.2
7	**3** (0.19)*	DMSO-d6	165	1.5	5	4.2
8	**4** (0.16)*	DMSO-d6	165	1.5	10.4	1.1
9	**1** (0.75)	DMSO-d6/EG (1:1)	165	0.5	22	0
10	**1**(0.75)	DMSO-d6/Sulfolane (1:1)	165	0.5	24	0
11	**1** (0.75)	EG	165	0.5	0	0
12	**1** (0.75)	Sulfolane	165	0.5	0	0
13	**1** (0.75)	DMSO/[BMIm]Cl (3:1)	165	0.5	4.1	trace
14	**1** (0.75)	[BMIm]Cl	165	0.5	0	0
15	**1** (7.5)	DMSO-d6	165	2	16	0

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16	**1** (1.8)	DMSO-d6	165	6	24	0
17	**1 (1.8)**	**DMSO-d6**	**165**	**24**	**28**	**0**
18	**1** (1.8)	DMSO-d6	180	0.5	4.6	0

Conditions: catalyst (20-200 mg), glucose (50 mg), solvent (1 mL total volume), 30 min to 24 h. Yields determined by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard and the peak at 9.55 ppm as the 5-HMF peak. * 10 mg of leather was used, leading to the differences in Cr content observed in the Table.

Utilization of **1-4** in DMSO-d6 at 165 °C for 30 minutes resulted in yields of 5-HMF ranging from 5 to 12% (Table 2, entries 5-8). No clear correlation between the yield and measured pH of the leather is apparent. Despite resulting in a modest yield, we further investigated **1** as a catalyst because **2** contained Cr(VI) (visualized by the CBZ test)[44] and with **4** the reaction mixture turned greenish/black, presumably due to contamination from the manufacturing process. Moreover, **1** contains the highest Cr content and the highest surface area (18.13 µg/mg and 14.8 m^2/g, respectively), as well as the highest Cr:S ratio (59% from EDS). Other solvents were evaluated in combination of DMSO. Ethylene glycol (EG) and sulfolane were selected because their high boiling point is suitable for the high-temperatures required.[59] Both solvents slightly increased the yield of 5-HMF when used in combination with DMSO-d6 (Table 2, entries 9-10). Notably, the reaction does not proceed in pure EG and in pure sulfolane (Table 2, entries 11-12), presumably to the very low solubility of D-glucose in these solvents and the catalytic role that DMSO-d6 plays in fructose conversion. ILs have been extensively used in combination with Cr(II) or Cr(III) catalysts in the transformations of glucose to 5-HMF[60,61] and, hence, we evaluated [BMIm]Cl as a co-catalyst in DMSO-d6 and as the solvent, but in both cases no enhancements in catalytic activity were observed (Table 2, entries 13-14). Consequently, further optimization resulted in the formation of 5-HMF in 28% (see Table 2, entries 15-18) using a prolonged reaction time (24 h) and higher catalyst loading (1.8 wt% Cr). After 24 h the liquid phase essentially consists of 5-HMF. The remainder of the by-products are insoluble in DMSO-d6 and presumably consist in humins that are formed from the thermal decomposition of 5-HMF.[62] Throughout the optimization process, co-products were observed (e.g. peaks in the ^{1}H NMR spectra that may be attributed to carbohydrates), and some of the by-products were identified by GC-MS and ^{1}H NMR spectroscopy, i.e. LGO and 2,5-diformylfuran, see Scheme 1). At short reaction times LGO is the main product (see entries 5-8 Table 2), and as the reaction progresses the LGO is consumed (6 to 24 h, see Figure S15 for a representative ^{1}H NMR spectrum, and Table 2, entries 16-18). However, the conversion of pure LGO into 5-HMF is very slow, and when LGO is employed as the substrate, it remains essentially unreacted after 2 h at 165 °C in DMSO-d6.[16,17] Similarly, at high catalyst loadings (0.75 wt% Cr, Table 1, entry 1), LGO is not observed, but it is observed when the Cr content is low (0.36 wt% Cr, entry 5). This is of interest since LGO is a valuable molecule that has attracted a lot of attention in recent years (building bloc, polar solvent ,etc.).[63]

After reaction, **1** was conveniently recovered by filtration and washed with EtOH and EtOAc, dried under vacuum, and reused. The catalyst was recycled with a distinct change in activity after the first cycle (see Table 3). The yield of 5-HMF decreases from 27% to 16% over the three cycles and the yield of LGO concomittantly increases from 0% to 12.8% yield. Formic acid (FA) was also present in the reaction mixture after the first recycling (peak at 8.1 ppm in the ^{1}H NMR spectrum, see Table 3 Figure S16). FA is typically formed during oxidative treatment of glucose and when air is present in the reaction mixture.[64,65] Typically, the transformation of glucose into FA requires a catalyst when air is used as the oxidant and is associated with the production of levulinic acid, but none was observed under our experimental conditions (see Figure S16). The oxidation product of 5-HMF, i.e. 2,5-diformylfuran, is also observed in very low quantities (< 1%). Both these products suggest that the oxidation pathway in DMSO also takes place.[66]

Table 3. Recycling experiments of **1**.

Entry	Cycle	Yield 5-HMF [%]	Yield LGO [%]	Yield FA [%]
1	**1**	27	0	1.1
2	**2**	16	4.4	1.6
3	**3**	16	12.8	2.4

Conditions: catalyst (50 mg), glucose (50 mg), solvent (1 mL total volume), 165 °C, 3 h. Yields determined by ^{1}H NMR spectroscopy using CH_2Br_2 as an internal standard and the peak at 9.55 ppm was used to quantify 5-HMF. The doublet of doublets at 7.53 ppm was used to quantify LGO and the peak at 8.14 ppm was used to quantify FA.

The recovered leather appeared less flexible after reaction, but was easily recovered although it became difficult to distinguish between the fibrous and smooth surface (SEM). The liquid phase of the reaction after the first reaction was analyzed by ICP-OES revealing leaching (approx. 7.5 ppm/mg leather) of the Cr contained into the leather, which rationalizes the observed decrease in 5-HMF yield upon reuse. Leaching is not unexpected since DMSO is an excellent solvent for the dissolution of metal ions, and leaching of Cr has been observed in previous reports. Cr loss from leather has even been observed in aqueous solutions with mostly Cr(III) species leaching from the native leather.[44] However, comparing the magnitude of leaching is difficult because leaching tests are not routinely reported in catalysis research papers.[67–69] Interestingly, as the Cr content decreases, LGO is formed in higher yields and is formed in nearly the same quantity as 5-HMF. This is consistent with the LGO being mainly observed after acid-catalyzed dehydration of glucose/cellulose. Despite the reduced catalytic activity of **1**, since there is an abundance of waste leather, fresh leather can be added to the reaction to maintain the yield of 5-HMF. Presumably, the loss of Cr in the catalyst is responsible for the change in selectivity of the reaction.

Based on the catalytic results obtained during optimization and recycling studies, we postulate that transformation proceeds following the two pathways presented in Figure 2, i.e. Cr-containing leather promotes the isomerization of glucose into fructose. The isomerization can occur via the Cr(III) mechanism and/or the acid-based mechanism since leather contains both Cr(III) and acid sites, and is presumably dominated by the former route as the reaction yield is sensitive to the concentration of Cr present.[58]

Conclusions

Here, we demonstrate the utilization of Cr-tanned leather as a heterogeneous catalyst for the synthesis of LGO and/or 5-HMF

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from glucose, since previous studies identified Cr as a privileged metal for this reaction. Non-shredded scrap leather pieces promote the transformation of glucose into 5-HMF in DMSO. It is remarkable that a material that is not specifically designed for catalytic applications results in yields comparable to those presented in recent reports (28% in this work vs 20 to 60% max yield in recent reports, see Table S1).[49–52] Notably, at low catalyst loadings LGO is also obtained in reasonable yields, and this is a particularly interesting product (solvent, chemical building block, etc[17]). We anticipate that other chemical reactions can be promoted by leather, such as ethylene polymerization, where Phillips catalyst (Figure 2) acts as a potent catalyst.[70]

Experimental Section

a. Materials and methods

Reagents were obtained from commercial sources and used as received. The leather samples were provided by shoe repair shops in Nyon and Geneva. The chromium content was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) on an ICP-OES 5100 (Agilent). Fourier-transform infrared (FT-IR) spectra were recorded on a PerkinElmer FT-IR 2000 instrument in the solid state. X-ray diffraction (XRD) was recorded on a D8 Bruker Discover equipped with a LynxEye 1D detector in Bragg Brentano geometry, using non-monochromated Cu-radiation. Samples of approx. 3 x 3 mm were placed on low background Si-crystal holders. Scanning electron microscopy (SEM) images were recorded on a Zeiss Nvision 40 Cross- Beam instrument with dual beam focus ion beam (FIB)/SEM based on GEMINI$ column. Brunauer-Emmett-Teller (BET) surface areas were determined on a Quantachrome Autosorb-IQ/MP-XR with N_2 as gas for analyte. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument. Gas chromatography – mass spectrometry (GC-MS) measurements were carried out on an Agilent 7890B instrument equipped with an Agilent 7000C MS triple quad detector and a capillary column from Agilent (l x d x f: 30 m x 0.25 mm x 0.25 µm) using N_2 as carrier gas.

Typical catalytic experiment

D-glucose (50 mg) and pieces of leather (20 - 200 mg) were placed in a 10 mL flask. The flask was then equipped with a magnetic stirrer. DMSO-d6 (1 mL) was added and the flask was then sealed. The reaction mixture was heated to the appropriate temperature (typically 165 °C) in a pre-heated oil bath. After the appropriate time (0.5 to 25 h), the mixture was allowed to cool to room temperature. The internal standard (CH_2Br_2) was added and a sample (0.5 mL) was removed, filtered and analyzed by ^{1}H NMR spectroscopy. The identity of 5-HMF was confirmed by GC-MS. LGO was identified by comparisons to reported ^{1}H and ^{13}C NMR spectra.[17] FA was identified by peak comparison in the ^{1}H NMR spectrum of a crude reaction mixture before and after the addition of pure, commercial FA.

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Keywords: Leather recycling – Chromium catalyst – Natural catalyst – 5-HMF production – Glucose conversion

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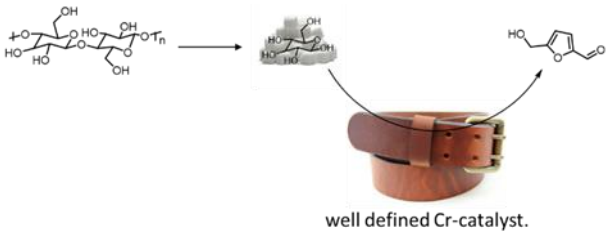

*Felix D. Bobbink, Zhangjun Huang, Florent Menoud, Paul J. Dyson**

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Leather promoted transformation of glucose into 5-hydroxymethylfurfural and levoglucosenone.

we demonstrate that leather acts as a heterogeneous catalyst in which chromium-ions are immobilized on collagen. Specifically, chromium-tanned leather catalyzes the transformation of D-glucose into levoglucosenone and 5-hydroxymethylfurfural in DMSO at 165 °C.

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