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Selective Aerobic Oxidation of 5-(Hydroxymethyl)furfural to 5-Formyl-2-furancarboxylic Acid in Water

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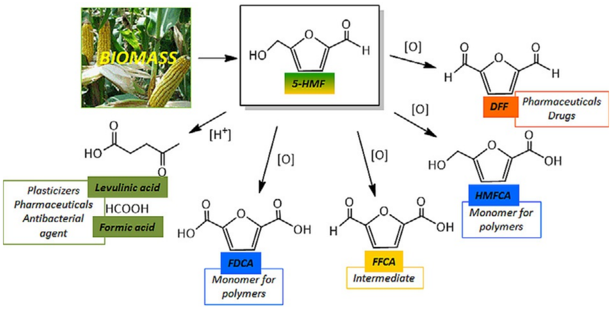
A simple, cheap, and selective catalyst based on copper/cerium oxides is described for the oxidation of 5-(hydroxymethyl)furfural (5-HMF) in water. An almost quantitative conversion (99%) with excellent (90%) selectivity towards the formation of 5-formyl-2-furancarboxylic acid, a platform molecule for other high value chemicals, is observed. The catalyst does not require any pretreatment or additives, such as bases, to obtain high yield and selectivity in water as solvent and using oxygen as oxidant. When a physical mixture of the oxides is used, low conversion and selectivity are observed. Air can be used instead of oxygen, but a lower conversion rate is observed if the same overall pressure is used, and the selectivity remains high. The catalyst can be recovered almost quantitatively and reused. Deactivation of the catalyst, observed in repeated runs, is due to the deposition of humins on its surface. Upon calcination the catalyst almost completely recovers its activity and selectivity, proving that the catalyst is robust.



Scheme 1. Molecules derived from 5-HMF and their use.

The increasing demand for energy is causing a rapid depletion of fossil carbon sources (coal, oil, gas) while increasing the atmospheric level of CO_2, necessitating the exploration of alternative carbon sources for chemicals and fuels, such as renewable carbon. Biomass, which is cheap and abundant in nature, is considered the most promising alternative to fossil carbons for the production of chemicals and, in some cases, fuels.[1] Because naturally available terrestrial biomass contains at least 75% carbohydrates, much emphasis has been placed on developing efficient approaches to transform biomass-sourced carbohydrates (C6 and C5) into value-added chemicals. Among the numerous chemical building blocks derived from renewable resources, 5-hydroxymethylfurfural (5-HMF)[2] is one of the most investigated (Scheme 1). 5-HMF can be obtained either from second-generation (cellulose-derived) glucose via isomerization to fructose, which is dehydrated to afford 5-HMF,[3] or even directly from cellulose.[4] It is the platform for a large variety of high value chemicals,[5] such as 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), 5-formyl-2-furancarboxylic acid (FFCA), 2,5-furandicarboxylic acid (FDCA), levulinic acid (LA), and formic acid (FA) (Scheme 1). Currently, several research groups are making efforts towards optimizing the synthesis of 5-HMF[6] and investigating the reactions in which it is involved.[7] 5-HMF has two functional groups, namely an alcoholic and an aldehydic moiety, which allows the production of a variety of chemicals via oxidation, hydrogenation, condensation, and reduction.[8]

Selective oxidation of 5-HMF to obtain DFF or FDCA has been much investigated owing to the versatility of these products as monomers, intermediates for pharmaceuticals, ligands, and others applications.[9] Because of difficulties with isolating the pure compound, the selective oxidation to FFCA has not attracted much attention despite its great potential as an intermediate. Oxidation of 5-HMF, due to the presence of two different reactive functionalities, can generate several derivatives that can find different applications.[10] A key objective of research, for a possible industrial application of processes,[11] is to find catalytic systems that are cheap, selective, and do not generate waste. In recent years, the use of oxygen or air as oxidant has been extensively investigated. Concerning the oxidation to DFF, metal oxides have been used with good yields of DFF. Using ruthenium over carbon nanotubes and *N*,*N*-dimethylformamide (DMF) as solvent,[12] yields of DFF of more than 90% have been reported. Yields of 80% have been reported using Au/MnO_2 in DMF as solvent.[13] $Ce_{1-x}Bi_xO_2$ can produce yields higher than 64% towards HMFCA in basic media.[14] Nitrogen-based compounds[12b, 15] play an important role when copper[16] catalysts are used, because of the capacity of this metal to coordinate to nitrogen ligands that enhance its reactivity. Gold[17] is the most-often used metal, because of its great activity and selectivity towards either DFF or FDCA. Sev-

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eral studies using this metal have been published, employing different kinds of solvents and in the presence or absence of bases. A 70:28 ratio of FFCA/FDCA was obtained when using a mixture of Pd/C and bismuth.[18] Yields of 98% toward FDCA were obtained with Pd/C[19] in a basic medium. Some studies suggest that the catalyst may undergo modification by action of the formed acids, causing poor selectivity; therefore, a basic medium is often used. However, bases may promote other adverse reactions that reduce the availability of the starting polyol. In a recent publication,[20] an excellent yield of FDCA (99%) from 5-HMF using hydrotalcite-supported gold nanoparticles, in water at 368 K, under atmospheric oxygen pressure without addition of base was reported. Nevertheless, there are only very few reports on the use of water as solvent, in absence of bases, despite its environmental friendliness. Reactions in water are difficult to control, because of the reactivity of the aldehydes that can be hydrated and produce oxidation or decomposition products. Considering this state of affairs, a selective oxidation of 5-HMF to FFCA, working in water and using dioxygen as oxidant, is missing.

We investigate catalysts built on mixed oxides targeting the selective oxidation of 5-HMF to any of the products from DFF to FDCA in Scheme 1. Herein, we present results on the oxidation of 5-HMF to FFCA using water as solvent. The oxidation is performed by cheap, earth-abundant metal oxides (copper/cerium) without addition of bases under mild conditions, using molecular oxygen or air as oxidant.[21]

We first performed the oxidation of 5-HMF with single oxides, CuO or CeO_2, either obtained commercially or synthesized in our laboratory. As shown in Table 1 the reaction with CuO (entry 1) achieves good selectivity towards FFCA (40%) with a moderate conversion (33%). CeO_2 (entry 2) shows a higher selectivity towards FFCA (76.6%), but a lower conversion. CuO is more active than CeO_2 and it also forms several other products, such as DFF, HMFCA and FDCA, which are not formed when CeO_2 is used. Performing the oxidation with the mixed oxide $CuO{\cdot}CeO_2$ leads to a quantitative conversion of 5-HMF (>99%, entry 5), high yield (90%), and good selectivity towards FFCA, without other oxidation or decomposition products, although H_2O was used as solvent and no external base was added to the reaction medium. When air is used instead of O_2, using the mixed oxide as catalyst, the reaction rate of oxidation of 5-HMF decreased (conversion = 13% after 3 h), but FFCA was formed as the sole product (selectivity = 99%).

Table 1. Catalytic oxidation of 5-HMF using various metal oxides as catalyst.[a]

Entry	Solid catalyst	t [h]	Conversion [%]	Yield/selectivity [%] DFF	HMFCA	FFCA	FDCA
1	CuO[b]	15	33.05	1.7/5.1	2.3/6.9	13.2/40	8.4/25.4
2	CeO_2[b]	15	19.9	0	0	15.3/76.6	0
3	CuO[c]	15	28.7	2.4/8.5	1.2/4.4	0	5.62/17.4
4	CeO_2[c]	15	21.3	0.1/0.6	0	18.9/88.7	0
5	$CuO{\cdot}CeO_2$	3	99	0	0	90/90	0
6	CuO + CeO_2[d]	15	5.3	0	1.2/22.6	3.2/60.4	0
7	No catalyst	24	93	0	7.4/7.9	0	0

[a] Reaction conditions: $[\text{5-HMF}]_i = 0.2$ M, 0.05 g of catalyst, 7 mL of water, $PO_2 = 0.9$ MPa, temperature = 383 K. [b] Commercial oxide. [c] Synthesized in our laboratory. [d] Physical mixture of CuO and CeO_2.

Interestingly, when a physical mixture of the two oxides in a 1:1 molar ratio is used (Table 1, entry 6), the conversion and yield are lower and the selectivity towards FFCA is much decreased. This implies that the mixed oxides form a new entity and not a simple mixture of oxides. Entry 7 shows that if the reaction is carried out in the absence of catalyst and in the same conditions (O_2 pressure and temperature) as used in entry 5, formic acid is obtained as major product after 24 h (selectivity 64%).

These results prompted us to make a comparative study of the acid–base properties of the single oxides and mixed oxides. Literature studies on the mechanism of 5-HMF oxidation using precious metal-catalysts demonstrate that the support must have a high basicity, in order to avoid the addition of external bases, and a moderate surface area.[22] To understand the importance of these parameters in our case, a surface characterization was carried out. Table 2 shows the Brunauer–Emmett–Teller (BET) surface area and acid and basic sites, expressed through the volume of NH_3 and CO_2 uptake and release, respectively. A comparison of entries 1 and 3 reveals that commercial and synthetized CuO have substantial different basicities, corresponding to markedly different catalytic activities (Table 1, entries 1 and 3). The lower basicity of the synthesized CuO (entry 3) as compared to the commercial one causes a lower activity towards the formation of FFCA. The properties shown by CeO_2 are more uniform when the commercial and synthesized oxides are compared (entries 2 and 4). The mixed oxide $CuO{\cdot}CeO_2$ has a higher basicity than the single oxides and a lower acidity than CeO_2. Hence, this simple mixture of the two oxides does not have reproducible values owing to the heterogeneity of the mixture. This indicates that the mixed oxide is not a simple mixture of oxides but really a new entity. Its BET area ($28.49\ m^2g^{-1}$) is intermediate between those of CeO_2 ($51–66\ m^2g^{-1}$) and CuO (ca. $10\ m^2g^{-1}$).

Table 2. BET surface area, basicity, and acidity of metal oxides.

Entry	Solid	CO_2 adsorbed [$mL\,g^{-1}$]	NH_3 adsorbed [$mL\,g^{-1}$]	BET surface area [m^2g^{-1}]
1	CuO[a]	0.25	0.23	9.53
2	CeO_2[a]	2.35	3.66	66.13
3	CuO[b]	0.053	0.23	10.67
4	CeO_2[b]	2.23	3.84	51.54
5	$CuO{\cdot}CeO_2$	3.15	2.24	28.49

[a] Commercial oxide. [b] Synthesized in our laboratory.

The new properties of the mixed oxide with respect to the parent oxides has a direct correlation to its catalytic activity. The increased basicity and good acidity of the catalyst result in an increased conversion yield (99%) and selectivity (90%) towards FFCA. Figure 1 shows the correlation between basic sites and selectivity towards FFCA, while Figure 2 correlates the number of acid sites to the selectivity. This evidences that

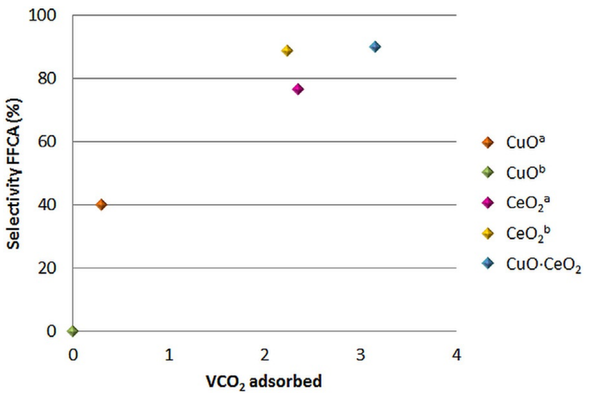

Figure 1. Selectivity toward FFCA vs V_{CO_2} adsorbed.

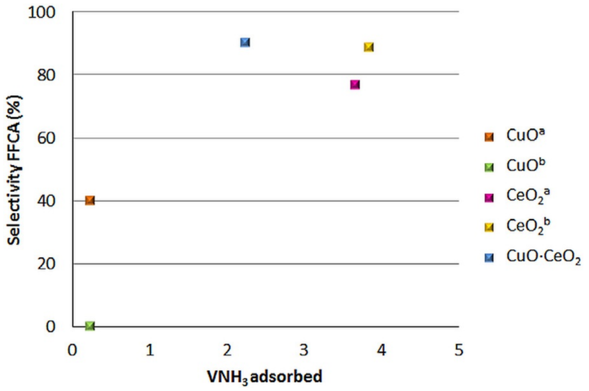

Figure 2. Selectivity toward FFCA vs V_{NH_3} adsorbed.

what matters is not the absolute value of a single property, namely "acidity" or "basicity", but the balance of the two with "basicity" prevailing on "acidity". Moreover, the ratio of strong basic sites to strong acid sites is important.

The maximum selectivity was obtained with the catalysts that have the highest basicity coupled to a significant acidity. Notably, solids with very poor acidity have poor selectivity and activity. Additionally, a large BET area is not recommended for a good activity

Preliminary analyses by X-ray diffraction (XRD) clearly show the presence of a single nanocrystalline phase in the mixed oxides. Peaks relevant to tenorite-CuO and cerianite-CeO_2 (according to the database of the Joint Committee on Powder Diffraction Standards (JCPDS)) are evident. Their shapes indicate the presence of a nanocrystalline phase. Such studies are still ongoing for an in-depth analysis of the change of XRD spectra with the composition of mixed oxides and for a comparison before and after reaction.

An elemental analysis of the catalyst, carried out by energy dispersed X-ray (EDX) spectroscopy, shows that the mixed oxide has a composition 56.1 % cerium and 43.71 % copper, with respect to calculated values of 69.68 % cerium and 30.32 % copper for a 1:1 CeO_2/CuO composition. However, the results discussed above show that mixed oxides can be an interesting solution to modulate the acid/base catalysts properties and drive the reaction in the direction of a target product working in water, with dioxygen (using air leads to more sluggish kinetics) as oxidant and in the absence of external bases. The oxidation of 5-HMF may involve either the oxidation of an aldehyde or that of the alcohol function. Figure 3 shows the evolution of the reaction with time: HMFCA is first formed (through the aldehyde moiety oxidation), and is then converted into FFCA.

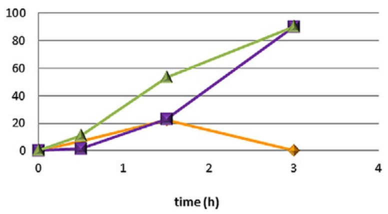

Figure 3. Kinetics of HMFCA and FFA formation and evolution of 5-HMF conversion. Catalyst: $CuO{\cdot}CeO_2$. Reaction conditions: $[5\text{-HMF}]_i = 0.2$ M, 0.05 g of catalyst, 7 mL of water, $P_{O_2} = 0.9$ MPa, $T = 383$ K. △: Conversion of 5-HMF; ◇: HMFCA yield; □: FFCA yield.

Our attempts to investigate the role of the reaction parameters in the oxidation to products other than FFCA, has allowed to discover and interesting concentration effect. In fact, when the initial concentration of 5-HMF in the reaction mixture was lowered from 2.0 M to 0.2 M, as Figure 4 shows, HMFCA was formed instead of FFCA, also if at moderate yield, but high selectivity. We also investigated whether or not the same catalyst would have been able to oxidize 5-HMF to FDCA. Attempts made by using the same reaction conditions used in the oxidation to FFCA and simply increasing the reaction time failed, as FFCA was decomposed on the long term and polymerization products were formed.

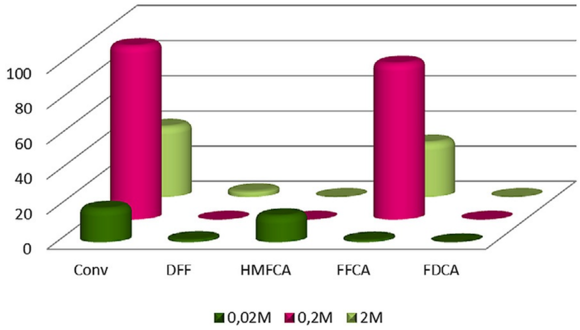

Figure 4. Conversion of 5-HMF and yield of different products with $CuO{\cdot}CeO_2$ as catalyst. The effect of changing the initial concentration of HMF is shown. Reaction conditions: $[5\text{-HMF}]_i = 0.02$ M, $[5\text{-HMF}]_i = 0.2$ M, and $[5\text{-HMF}]_i = 2$ M, 5 mL of H_2O, 0.05 g of catalyst, $P_{O_2} = 0.9$ MPa.

The catalyst recovery and reusability was also tested using the mixed oxide $CuO{\cdot}CeO_2$ (Figure 5). In a typical test, the catalyst was allowed to react for 3 h, and then filtered, washed with water (7 mL) three times, and reused in a new run. The activity of the catalyst decreased with increasing the number of cycles (1–4 in Figure 5) most probably because humins gen-

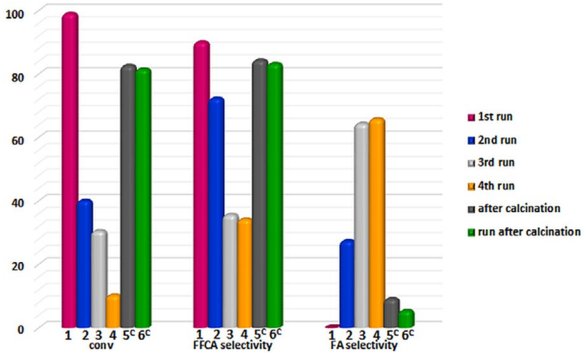

Figure 5. Catalyst reusability in the oxidation of 5-HMF using CuO·CeO$_2$.

erated in the reaction may remain attached to the solid. We noted a change of the color of the catalyst in its deactivated form. When the deactivated catalyst was calcined at 823 K for 3 h (5^c in Figure 5), the catalytic activity was almost recovered at comparable selectivity. This proved true also in additional runs (6^c in Figure 5), also. Notably, when the catalyst is deactivated, a rapid degradation of 5-HMF to FA takes place. Interestingly, the catalyst was recovered at 99% and EDX analysis of the catalyst after the runs confirmed that there was no significant metal loss after the reaction: only traces of copper were observed. We conclude that the catalyst is deactivated by deposition of organic species on its surface, more than by leaching: the activity can be recovered by calcination that burns the organics and cleans the surface.

Such results are of interest because they indicate that specialized catalysts are needed for producing different oxidation products of 5-HMF. While a copper/cerium mixed oxide is a good catalyst for the oxidation of 5-HMF to HMFCA and FFCA, we have isolated DFF with high selectivity ($\geq$99%) when working with other mixed oxides.[23] Our studies towards the discovery of the best conditions for a selective and efficient conversion of 5-HMF into FDCA, an interesting substitute of terephtalic acid, are on-going.

In conclusion, a cheap mixed oxide CuO·CeO$_2$ was prepared by high energy milling (HEM), and is highly active towards the selective conversion of 5-hydroxymethylfurfural (5-HMF) into 5-formyl-2-furancarboxylic acid (FFCA; 99% conversion yield, 90% selectivity) in water, using molecular oxygen as oxidant and without external base. Oxidation in air was also effective, but with slower kinetics. The dependence of the activity and selectivity on the acid–base sites is demonstrated. The basicity of the catalysts drives the activity and selectivity. High acidity results in a poor activity, but if the acidity is too low, the catalyst is not active. The correct ratio of acid/base sites can be tuned by choosing the correct oxides, that is, by using a mixed oxide. The results presented here are of use for the further rational design of earth-abundant mixed oxide catalysts, and can drive the oxidation of cellulose-derived platform molecules for the production of fine chemicals and monomers.

Experimental Section

Materials: Cerium(IV) ammonium nitrate $\geq$98% (by titration); cerium(IV) oxide nanopowder, $<$25 nm particle size (BET), 99.95% trace rare earth metals basis; copper(II) nitrate trihydrate puriss., 99–104%; copper(II) oxide 99.9% trace metals basis; 2,5-furandicarboxaldehyde $\geq$97%; 5-formyl-2-furoic acid 99%; 5-hydroxymethyl-2-furancarboxylic 99%, were ACS-grade reagents purchased from Sigma–Aldrich. 5-(Hydroxymethyl)furfural $\geq$99% was prepared as reported earlier.[6a]

Analytical methods: 5-HMF and derivatives were analyzed by using a Jasco HPLC equipped with a UV detector at 284 nm and a Phenomenex Rezex RHM monosaccharide H+(8%) 300$\times$7.8 mm column at 343 K. A 0.005 N solution of sulphuric acid was used as the mobile phase at a 0.5–0.9 mL min^{-1}. The concentration of 5-HMF and reaction products were determined by using a RI detector. Surface characterization of the catalysts was carried out by using a Pulse ChemiSorb 2750 Micromeritics instrument. Analyses of the acid/basic sites was carried out using NH$_3$ or CO$_2$, respectively, as probe-gas using 100 mg of catalyst and He as carrier gas (30 mL min^{-1}). The samples were pretreated under N$_2$ (30 mL min^{-1}) flow and 673 K. The Pulse Chemisorb was performed with NH$_3$ or CO$_2$. BET area was determined using N$_2$/He as a carrier gas at 273 K followed by heating up to 923 K. X-ray powder diffraction (XRD) patterns of the samples were determined using a Rigaku powder diffractometer (Cu$_{K\alpha}$). All XRD patterns were collected in the 2θ range 10°–120° at a scanning rate of 0.008° s^{-1}. The elemental analysis of CuO·CeO$_2$ was carried out by using a Shimadzu 720P Energy Dispersive X-Ray spectrometer and a calibration curve made with the standard single oxide, CuO and CeO$_2$.

Synthesis of single oxides CuO or CeO$_2$: 3 mmol of copper(II) nitrate trihydrate (0.72 g) or cerium(IV) ammonium nitrate (1.64 g), were calcined for 3 h at 823 K giving a dark solid (CuO) or pale-yellow solid (CeO$_2$). The solids were transferred into a flask and stored under N$_2$ to prevent uncontrolled surface deterioration prior to catalysis.

Synthesis of CuO·CeO$_2$: 3 mmol of cerium(IV) ammonium nitrate (1.64 g) and 3 mmol of copper(II) nitrate trihydrate (0.72 g) were mixed in a HEM apparatus, pulverized at 790 rpm during 1 h with pauses of 1 min every 15 min. The pale green mixture was calcined for 3 h at 823 K giving a dark-brown solid that was transferred into a flask under N$_2$ atmosphere.

Typical experimental procedure: The kinetics of conversion of 5-HMF at a fixed temperature (383 K) were studied in a 50 mL stainless-steel reactor equipped with a withdrawal valve and an electrical heating jacket. 0.177 g of 5-HMF was dissolved in 7 mL of distilled water in a glass reactor, in which 0.05 g of the catalyst under study and a magnetic stirrer were placed. The glass reactor was then transferred into the reactor that was closed and purged three times with O$_2$. It was charged with 0.9 MPa of oxygen and heated to the reaction temperature (383 K). At fixed intervals of time, stirring was stopped; a sample was withdrawn and analyzed by HPLC.

Recovery and reuse of the catalyst as such: The mixed oxide catalyst was recovered by filtration at the end of the first run, washed with water (3$\times$7 mL), and reused in a second run. These operations were repeated three times on the same catalyst. Both conversion and selectivity were reduced in each next run. (Figure 5).

Recovery and reuse of the catalyst after calcination: The catalyst was recovered after the first run, washed with water (3$\times$7 mL) and calcined at 823 K for 3 h. This operation was repeated two times. The catalyst almost recovered its activity and selectivity. (Figure 5)

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Keywords: heterogeneous catalysis · metal oxides · oxidation · renewable resources · water chemistry

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