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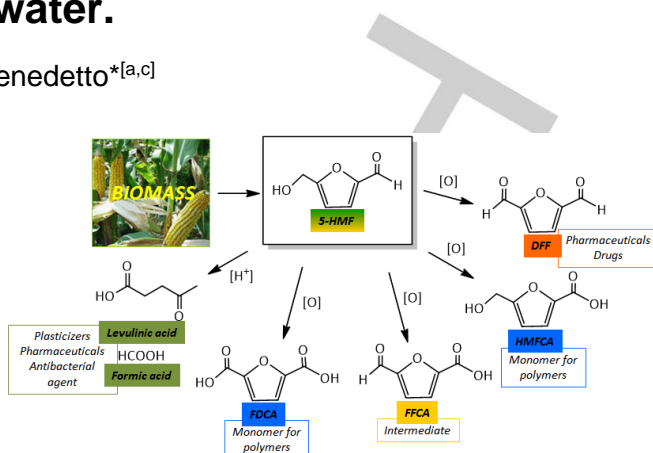
Selective aerobic oxidation of 5-(hydroxymethyl)furfural to 5-formyl-2-furancarboxylic acid in water.

Maria Ventura,[a] Michele Aresta,[b] and Angela Dibenedetto*[a,c]

Abstract: In the present work a simple, cheap and selective catalyst based on Cu/Ce oxides, is described for the oxidation of 5-(hydroxymethyl)furfural 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, was observed. The catalyst does not need any pre-treatment or additives, such as bases, for obtaining high yield and selectivity in water as solvent and using oxygen as oxidant. If a mere physical mixture of the oxides was used, both low conversion and selectivity were 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: only traces of Cu are found in solution. Deactivation of the catalyst is anyway observed in repeated runs, due to the deposition of humins on its surface. In fact, if the catalyst is calcined after the first run, it almost recovers its activity and selectivity. This is true also for additional runs. We conclude that the catalyst is robust and deactivation is due to the deposition of organics on its surface.

The increasing energy demand is causing a rapid depletion of fossil carbon (coal, oil, gas) while increasing the CO_2 atmospheric level, making necessary to explore alternative carbon-sources for chemicals and fuels, such as renewable carbon. Biomass, that is cheap and abundant in nature, is considered the most promising alternative to fossil carbon for the production of chemicals and, in some cases, fuels.[1] As naturally available terrestrial biomass contains at least 75% carbohydrates, much interest 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 and formic acid (FA) (Scheme 1). Currently, several research groups are making efforts in optimizing the synthesis of 5-HMF[6] and investigate the reactions in which it is involved.[7] 5-HMF has two functional groups, namely an alcoholic and an aldehydic moiety, which allow the production of a variety of chemicals *via* oxidation, hydrogenation, condensation and reduction.[8]

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

Selective oxidation of 5-HMF to obtain DFF or FDCA has been much investigated due to their versatility in the use as monomers, intermediates for pharmaceuticals, ligands and others applications.[9] Owing to the difficulties of isolation, the selective oxidation to FFCA has not attracted much attention, despite it has a great potential as intermediate. 5-HMF oxidation, due to the presence of two different reactive functionalities, can generate several derivatives that can find different applications.[10] The key objective of research, for a possible industrialization of processes,[11] is finding catalytic systems which 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 quite interesting yield of DFF. Using Ru over carbon nanotubes,[12] yields more than 90% towards DFF, using DMF as solvent, was reported. Yield of 80% has been reported using Au/MnO_2[13] in DMF as solvent. $Ce_{1-x}Bi_xO_2$[14] can produce yields higher than 64% towards HMFCA in basic media. N-based compounds[12b, 15] play an important role when Cu[16] catalysts are used, for the capacity of such metal to coordinate to N-ligands that enhance its reactivity. Au[17] is the most used metal, because of the great activity and selectivity towards DFF or FDCA formation. Several studies have been reported about this metal, using different kinds of solvents and in presence or absence of bases. A ratio of 70/28 FFCA/FDCA has been obtained when using a mixture of Pd/C and Bi.[18] Yields of 98% toward FDCA were obtained with Pd/C[19] in a basic medium. Some studies suggest that catalyst may undergo modification by action of the formed acids, causing a poor selectivity. So a basic medium is used. Nevertheless, bases may promote other negative processes 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 is documented. Nevertheless, there are only a very few reports about the use of water as solvent, in absence of bases, despite its environmental friendliness. As a matter of fact, the reactions in water are difficult to control, because of the reactivity of the aldehydes that can be hydrated and produce more oxidation or decomposition products. In this landscape, the selective oxidation of 5-HMF to FFCA, working in water and using dioxygen as oxidant, is

missing.

We have started a research on catalysts built on mixed oxides targeting the selective oxidation of 5-HMF to any of the products from DFF to FDCA in Scheme 1. In this paper, we present the results of our studies on the 5-HMF oxidation to FFCA, using water as solvent and performing the oxidation with cheap, Earth crust abundant metal oxides (Cu/Ce) without addition of bases under mild conditions, using O_2 or air as oxidant.[21]

The oxidation of 5-HMF with single oxides, CuO or CeO_2, either commercial or synthesized in our laboratory, was first performed. 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 so that it also originates several other products such as DFF, HMFCA and FDCA, not formed when CeO_2 is used (Table 1). When the oxidation is performed with the mixed oxide $CuO \cdot CeO_2$, it leads to a quantitative conversion of 5-HMF (>99%, Entry 5, Table 1), high yield (90%) and selectivity towards FFCA, with absence of other oxidation or decomposition products, although H_2O was used as solvent with no addition of an external base to the reaction medium. When air was 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 %). Interestingly, if a physical mixture of the two oxides in a 1:1 molar ratio is used (Entry 6), the conversion and yield is lower and the selectivity towards FFCA much decreased. This clearly shows that the mixed oxides are a new entity and not a simple mixture of oxides. Entry 7 in Table 1 shows that if the reaction is carried out in absence of catalyst and in the same conditions of O_2 pressure and temperature as used in Entry 5, after 24 h formic acid is obtained as major product (selectivity=64%).

Table 1. Catalytic tests in the oxidation of 5-HMF using various metal oxides as catalyst.

Entry	Solid	Time(h)	Convers(%)	Yield/Selectivity %			
				DFF	HMFCA	FFCA	FDCA
1	CuO[a]	15	33.05	1.7/5.1	2.3/6.9	13.2/40	8.4/25.4
2	CeO₂[a]	15	19.9	0	0	15.3/76.6	0
3	CuO[b]	15	28.7	2.4/8.5	1.2/4.4	0	5.62/17.4
4	CeO₂[b]	15	21.3	0.1/0.6	0	18.9/88.7	0
5	CuO·CeO₂	3	99	0	0	90/90	0
6	CuO+CeO₂[c]	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

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

We have made a comparative study of the acid-base properties of the single oxides and mixed oxides.
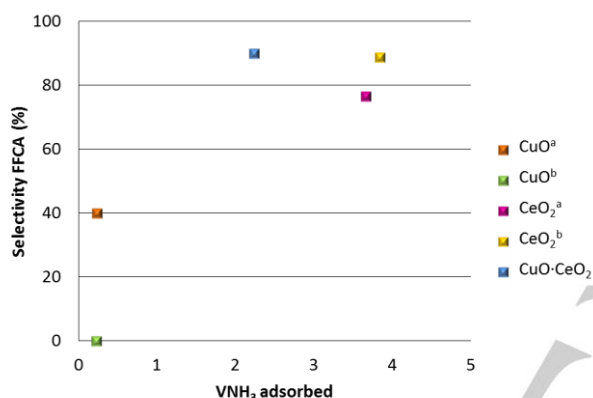
Studies available in the literature about the mechanism of 5-HMF oxidation using precious metal-catalysts demonstrate that the support must have a high basicity, in order to avoid the addition of external bases, and a moderate surface area.[22] In order to understand the importance of such parameters in our case, a surface characterization has been carried out. Table 2 shows BET surface area, acid and basic sites expressed through the volume of NH_3 and CO_2 up-taken and released, respectively. A comparison of Entries 1 and 3 in Table 2 shows that commercial and synthetized CuO have substantial different basicity that corresponds to a quite different catalytic activity (Entries 1 and 3 in Table 1). The lower basicity of the synthesized CuO (Entry 3) with respect 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 in Table 1 or 2). The mixed oxide $CuO \cdot CeO_2$ has a higher basicity than the single oxides and a lower acidity than CeO_2. A simple mixture of the two oxides has not reproducible values due to the heterogeneity of the mixture. This shows that the mixed oxide is not a simple mixture of oxides but really a new entity. Its BET area (28.49 m^2/g) has an intermediate value between that of CeO_2 (51-66 m^2/g) and that of CuO (ca. 10 m^2/g)

Table 2. BET surface area basicity and acidity of CuO, CeO_2 and $CuO \cdot CeO_2$

Entry	Solid	V of CO₂ adsorbed (mL/g)	V of NH₃ adsorbed (mL/g)	BET surface area (m²/g)
1	CuO[a]	0.25	0.23	9.53
2	CeO₂[a]	2.35	3.66	66.13
3	CuO[b]	0.053	0.23	10.67
4	CeO₂[b]	2.23	3.84	51.54
5	CuO·CeO₂	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 have a direct correlation with the catalytic activity. The increased basicity and good acidity of the catalyst turn into 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. It is evident that 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 *strong basic sites* to *strong acid sites* is important.

Figure 1. Selectivity toward FFCA vs VCO₂ adsorbed.

Figure 1 plot: Selectivity FFCA (%) vs VCO_2 adsorbed. Legend: CuO[a], CuO[b], CeO₂[a], CeO₂[b], CuO·CeO₂
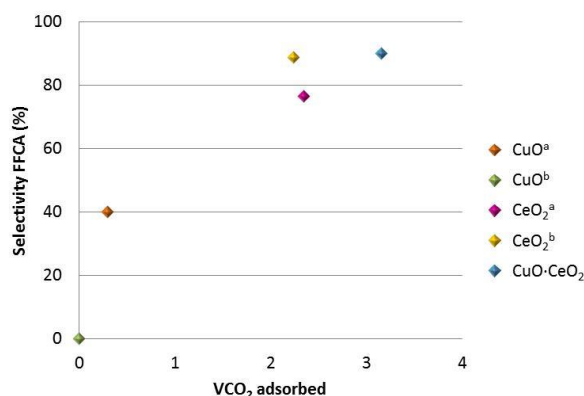
Figure 2. Selectivity toward FFCA vs VNH₃ adsorbed.

Figure 2 plot: Selectivity FFCA (%) vs VNH_3 adsorbed. Legend: CuO[a], CuO[b], CeO₂[a], CeO₂[b], CuO·CeO₂

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

Preliminary XRD analyses clearly show the presence of a single nanocrystalline phase in the mixed oxides. Peaks relevant to tenorite-CuO and cerianite-CeO₂ (JCPDS data base) are well evident. Their shape indicates 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. The results will be presented in a full paper.

The elemental analysis of the catalyst, carried out by Energy Dispersed X-Ray Spectroscopy (EDX), shows that the mixed oxide has a composition 56.1% Ce and 43.71% Cu, with respect to calculated values %Ce = 69.68 and %Cu = 30.32 for a 1:1 CeO₂-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 has a lower kinetics) as oxidant and in 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), which is then converted into FFCA.

Figure 3. Kinetics of HMFCA and FFA formation and evolution of 5-HMF conversion is shown. CuO·CeO₂ is used as catalyst.

Reaction conditions: [5-HMF]ᵢ=0.2 M, 0.05 g of catalyst, 7 mL of water, PO₂ = 0.9 MPa, temperature = 383 K . Conversion of 5-HMFΔ; HMFCA yield◊; FFCA yield □.
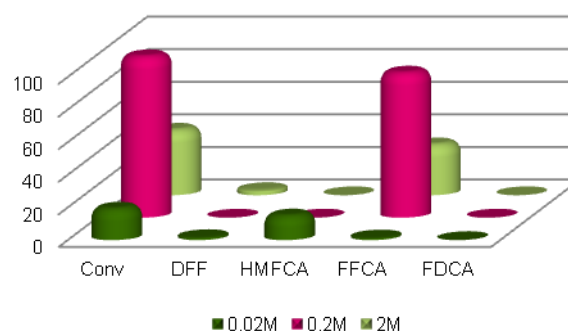

Figure 3 plot: concentration/yield (%) vs time (h).
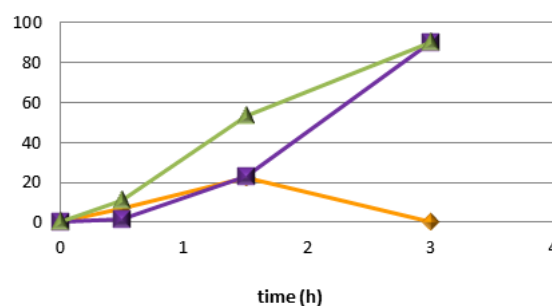
Our attempts to investigate the role of the reaction parameters in the oxidation to products other than FFCA, has allowed to discover and interesting "concentration effect". In fact, when the initial concentration of 5-HMF in the reaction mixture was lowered from 2.0 M to 0.2 M, as Fig. 4 shows, HMFCA was formed instead of FFCA, also if at moderate yield, but high selectivity.

We have also investigated whether or not the same catalyst would have been able to oxidize 5-HMF to FDCA. The 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·CeO₂ as catalyst. The effect of changing the initial [HMF] is shown.

Reaction conditions: [5-HMF]ᵢ=0.02M, [5-HMF]ᵢ=0.2M, and [5-HMF]ᵢ=2M, 5 mL of H₂O, 0.05 g of catalyst, PO₂= 0.9 MPa.

Figure 4 bar chart: categories Conv, DFF, HMFCA, FFCA, FDCA. Legend: 0,02M, 0,2M, 2M

The catalyst recovery and reusability was also tested using the mixed oxide CuO·CeO₂ (Fig. 5). In a typical test, the catalyst was allowed to react for 3 h, was then filtered, washed with water (7 mL) three times, and reused in a new run.

Figure 5. Reusability studies in the oxidation of 5-HMF using CuO·CeO₂ as catalyst.
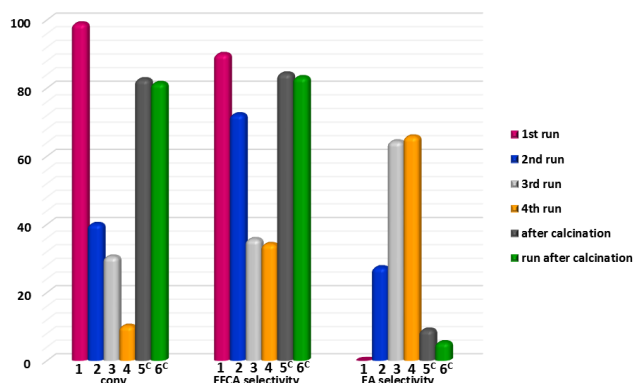
The experimental results show that the catalytic activity of the catalyst decreases with the increase of the number of cycles (1-4 in Fig. 5) most probably because humins generated in the reaction may remain attached to the solid. As a matter of fact we have observed a change of the color of the catalyst in its deactivated form. If the deactivated catalyst is calcined at 823 K for 3 h (5^c in Fig. 5), the catalytic activity is almost recovered at almost the same selectivity. This is true also in additional runs (6^c in Fig. 5). Noteworthy, when the catalyst is deactivated, a rapid degradation of 5-HMF to FA takes place. Interestingly, the catalyst is anyway recovered at 99% and the EDX analysis of the catalyst after the runs confirmed that there is no significant metal loss after the reaction: only traces of copper were observed. We conclude then, 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 as they say that specialized catalysts are needed for producing different oxidation products of 5-HMF. While Cu/Ce mixed oxide is a good catalyst for the oxidation of 5-HMF to HMFCA and FFCA, we have isolated DFF with high selectivity (≥99%), working with other mixed oxides.[23] Our studies continue towards the discovery of the best conditions for a selective and efficient conversion of 5-HMF into FDCA, an interesting substitute of terephtalic acid.

The cheap mixed oxide CuO·CeO₂ prepared by High Energy Milling (HEM) has high activity for the selective conversion of 5-HMF into FFCA (99% conversion yield, 90% selectivity) in water, using O₂ as oxidant and without external base. Air is also effective, but the kinetics is lower. The dependence of the activity and selectivity on the acid-basic sites is demonstrated. The basicity of the catalysts drives the activity and selectivity, a high acidity results in a poor activity, but if the acidity is too low, the catalyst is not active. The correct ratio of acid/basic sites can be built by choosing the correct oxides, which will generate the mixed oxide. The results presented here are expected to be useful for further rational design of earth-abundant mixed oxides catalysts, which can drive the reaction of oxidation of cellulose derived platform molecules for the production of useful fine-chemicals or monomers for polymers.

Experimental Section

(A)Materials.

Cerium (IV) ammonium nitrate ≥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 ≥97%; 5-formyl-2-furoic acid 99%; 5-hydroxymethyl-2-furancarboxylic 99% , were ACS grade reagents purchased from Sigma Aldrich. 5-(Hydroxymethyl)furfural ≥99% was prepared as we reported before.[6a]

(B) 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%) 300x7.8mm at 343 K. A 0.005 N solution of sulphuric acid was used as the mobile phase. The flow rate 0.5-0.9 mL/min. The concentration of 5-HMF and reaction products was determined using a RI detector. Surface characterization of the catalysts was carried out by using the Pulse ChemiSorb 2750 Micromeritics instrument. Analyses of the acid/basic sites were carried out using NH₃ or CO₂, respectively, as probe-gas using 100 mg of catalyst. The samples were pre-treated under N2 (30 mL min⁻¹) flow and 673 K. The Pulse Chemisorb was performed with NH₃ or CO₂ gas using He as carrier gas (30 mL min⁻¹). TPD were performed under He flow at 30 mL min⁻¹. BET area was determined using N₂/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-Kα). All XRD patterns were collected in the 2θ range 10–120° at a scanning rate of 0.008°/s. The elemental analysis of CuO·CeO₂ was carried out using a Shimadzu 720P Energy Dispersive X-Ray Spectrometer and using the calibration curve made with the standard single oxide, CuO and CeO₂.

(C) Catalysis preparation.

C.1. Synthesis of single oxides CuO or CeO₂:

3 mmol of Copper (II) nitrate trihydrate (0.72 g) or cerium (IV) ammonium nitrate (1.64 g), were calcined for three hours at 823 K giving a dark solid for CuO or pale-yellow solid for CeO₂. The solids were transferred into a flask and store under N₂ atmosphere to prevent uncontrolled surface deterioration prior to catalysis.

C.2. Synthesis of CuO·CeO₂:

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 1h 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 N₂ atmosphere.

(D) Typical experimental procedure.

The kinetics of conversion of 5-HMF at a fixed temperature (383 K), was studied in a 50 mL stainless-steel reactor equipped with a withdrawal valve and an electrical heating jacket. 0.177g of 5-HMF were 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 O₂. 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.

(E) 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 (3x7 mL) and reused in a second run. Such operation was repeated three times on the same catalyst. Both conversion and selectivity were reduced in each next run. (Fig. 5)

(F) Recovery and reuse of the catalyst after calcination.

The catalyst was recovered after the first run, washed with water (3x7 mL) and calcined at 823 K for 3 h. Such operation was repeated two times. The catalyst almost recovered its activity and selectivity. (Fig. 5)

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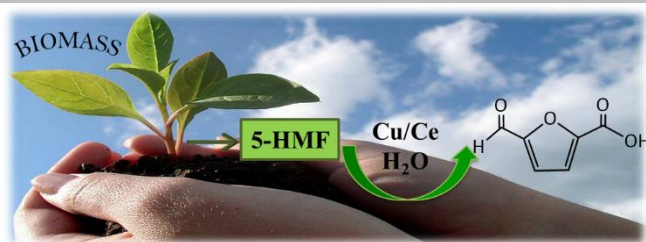
Maria Ventura, Michele Aresta and Angela Dibenedetto*

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Selective aerobic oxidation of 5-(hydroxymethyl)furfural to 5-formyl-2-furancarboxylic acid in water.

The cheap mixed oxide $CuO \cdot CeO_2$ prepared by a simple method has high activity for the selective conversion of 5-HMF into FFCA (99% conversion yield, 90% selectivity) in water, using O_2 as oxidant and without any external additives.