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COMMUNICATION

Tunable mixed oxides based on CeO_2 for the selective aerobic oxidation of 5-(hydroxymethyl) furfural to FDCA in water

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Chemicals derived from 5-HMF,[1a] via selective oxidation of its pending arms are becoming increasingly important due to their applications.[1b] This paper discusses the use of Earth crust abundant new mixed oxides based on CeO_2 able to perform the selective oxidation of 5-HMF into 2,5-furandicarboxylic acid (99%), in water, using oxygen as oxidant.

Petroleum products, including chemicals, plastics, and synthetic materials used in daily life, represent about 90% of the world‘s organic chemicals. Replacement of fossil carbon with renewable carbon will most likely play a key role in sustaining the growth of the chemical industry.[2] The transformation of renewable biomass into chemicals is becoming more and more attractive as a way to avoid the aggravation of CO_2 emission and diversify sources of energy and materials.[3] The development of cost-effective catalytic processes adapted to the molecular structure of functionalized biomass-sourced molecules is a challenging task.[4] 2,5-Furandicarboxylic (FDCA) acid has been described as one of the 12 key platform molecules derived from biomass by the US Department of Energy, because of its potential as replacement of terephthalic acid for the production of substitutes of poly(ethene-terephthalate) (PET).[1] FDCA can be prepared by oxidation of 5-HMF (Figure 1), prepared in turn by acid-catalyzed dehydration of fructose[5] or even directly from cellulose.[6] 5-HMF can be oxidized to FDCA with stoichiometric oxidants,[7] metal catalysts,[8] or enzymes.[9] With the objective to minimize waste, the heterogeneous catalytic oxidation of 5-HMF with oxygen or air in water is much attractive. In such case, Au,[10] and Pt,[11] usually supported on TiO_2 or ZrO_2 or even C, and combined with a base as additive are used Ru/C has been shown to afford 80% as maximum of selectivity under oxygen pressure.[12] Catalysts such as Cu or V immobilized onto costly amino functionalized SBA-15 have also been studied, but no more than 28.8% of selectivity towards FDCA was obtained.[13] Additionally, when a cheaper support was used the stability of the catalyst was not good, as for example with Ru/MgOLa$_2$O$_3$.[12b] Quantitative yields were obtained but high leaching of MgO was detected making such heterogeneous catalyst not very useful. DFF (Fig. 1) is another platform chemical, used for the synthesis of drugs or high added value products.[14] Because of its poor solubility in water, classically DFF is synthesized using organic solvents.[15] Nevertheless, the use of water is interesting as DFF can separate from the reaction medium at the end of the reaction.[18] As mentioned above, expensive metals, such as Ru, Pt, or Au, have often been used.[16]

Recently, layered double hydroxides Mn0.70Cu0.05Al0.25OH, whose structural properties were not fully disclosed, have been reported,[17] resulting among the most efficient catalysts for the formation of DFF in water.[18] In fact, 64.2% of selectivity was achieved (30.2% conversion) using Cu/Cr/V-doped MnO_2 catalyst and O_2 as oxidant getting better results when organic solvents were used.[19]

We have recently studied the selective oxidation of 5-HMF towards FFCA (formyl-furan-carboxylic acid) using non-noble catalysts made of CuO and CeO_2,[20] or towards DFF or HMFCA using the mixed oxide MgO·CeO_2.[18b] Both above catalysts were not able to further oxidize the intermediates to FDCA. Therefore, we have made an effort to find the correct conditions and the appropriate mixed oxides to achieve a significant conversion of 5-HMF with high selectivity towards FDCA. A literature survey reveals that the oxidation of 5-HMF into FDCA can be achieved using solids based on Mn,[21] which have the serious drawback of being soluble in water.

In the present paper, we discuss the oxidation of 5-HMF using heterogeneous catalysts based on CeO_2 mixed with metal oxides with strong redox properties such as MnO_2 and CuO, in absence of external bases, under mild conditions, using molecular oxygen as oxidant in water. It is worth recalling that external bases are often used to enhance the deprotonation of the alcoholic moiety or hydration of the aldehyde that makes

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easier the oxidation of the above mentioned moieties. Our strategy is to tune the acid-basic properties of the catalysts, by controlling the n_b/n_a ratio (strong basic over strong acid sites) avoiding the addition of bases, thus reducing costs and waste production.

The catalytic activity of the single oxides was first evaluated. In Table 1 are presented the results of 5-HMF conversion and the product distribution using various single oxides as catalysts.

Table 1. Catalytic tests in the oxidation of 5-HMF using single oxides as catalysts

	cat	t (h)	T (K)	Conv. (%)	Selectivity (mol %)					
					DFF	HMFCA	FFCA	FDCA	FA	LA
1	CeO_2	15	383	21.3	0.6	0	88.7	0	0	0
2	CuO	15	383	33.0	5.1	6.9	40	25.4	0	0
3	MnO_2[a]	12	403	99.0	0	0	23.5	75.5	0	0.8

Reaction conditions: $[5\text{-HMF}]_i$=0.2 M, 0.05 g of catalyst, 7 mL of water, PO_2 = 0.9 MPa. [a]not effective at 383 K. At T > 403 K degradation products were formed. LA is levulinic acid, FA is formic acid.

As we have reported before[20], CeO_2 and CuO produce (Table 1, Entries 1, 2) FFCA as the main product of oxidation, even if with different selectivity. When a stronger oxidant as MnO_2 was used, FDCA was formed as the main oxidation product with a yield of 75.5%, together with FFCA (23.5%) and small amounts of levulinic acid (LA) (Table 1, Entry 3). MnO_2 could, thus, be a good candidate to perform the oxidation of 5-HMF into FDCA, but its high dissolution in water makes it not appropriate as a heterogeneous catalyst: a loss of 75% of the original solid catalyst was detected by EDX and Flameless Atomic Absorption Spectrometry-FLAAS (see Experimental Section)

The catalysts were also characterized for their S-BET surface area; moreover weak and strong acidic/basic sites calculated from the NH_3/CO_2 thermo-desorption curves are reported in Table 2.

The strength of different acidic/basic sites is divided into three categories:[22] i) weak basic sites are the hydroxyl groups present on the surface: thermo-desorption occurs at 290-430 K; ii) medium basic are M=O moieties: desorption occurs at 430-670 K; iii) strong basic are isolated O^{2-} species: desorption above 670 K. Medium- and strong-basic sites are most likely responsible of the catalytic activity of the oxides and, thus, have been summed together in this work. The same classification has been made for the acid strength: in particular, weak acidity is assigned to the protons of the OH moieties present on the surface of the oxides, while strong acidity is attributed to the Lewis acids M^{n+}.[23]

Our previous studies have shown that, supposed that a catalyst has the correct oxidation potential, its activity can be influenced by the ratio n_b/n_a.[20] Table 1 shows that the nature of the product depends on the catalyst used: only MnO_2 is able to afford FDCA.

Table 2. BET Surface and Basic/Acidic Sites Strength of single and mixed oxides

Entry	Solid	Total VCO_2 adsorbed (mL/g)	Weak CO_2 adsorption (mL/g)	Strong CO_2 adsorption (mL/g)	Total VNH_3 adsorbed (mL/g)	Weak NH_3 adsorption (mL/g)	Strong NH_3 adsorption (mL/g)	BET surface area (m^2/g)	nb/na
1	CeO_2	2.34	1.01	1.32	3.05	1.26	1.80	66.12	0.73
2	CuO	0.037	0.012	0.025	0.24	0.012	0.23	10.67	0.11
3	MnO_2	12,64	1,76	10,74	6,7	0.84	5,86	47.05	1.83
4	$MnO_2{\cdot}CeO_2$[a]	0.52	0.051	0.48	0.98	0.041	0.84	25.45	0.57
5	$MnO_2{\cdot}CeO_2$[b]	0.43	0.083	0.35	1.19	0.025	1.16	19.96	0.30
6	$MnO_2{\cdot}CeO_2$[c]	0.19	0.094	0.18	1.51	0.020	1.37	23.10	0.13
7	$CuO{\cdot}MnO_2{\cdot}CeO_2$	0.45	0.065	0.39	1.86	0.12	1.74	33.09	0.22
8	$1.5\ CuO{\cdot}MnO_2{\cdot}CeO_2$	0.44	0.063	0.37	1.80	0.10	1.70	28.00	0.20

[a.] Calcined at 723K; [b.] calcined at 823 K; [c.] calcined at 923 K.

The S-BET surface area (Table 2) follows the order: CuO< MnO_2<CeO_2. It is not possible to make any correlation with the activity of the catalysts, implying that BET surface area is not a dominant factor in driving the selectivity in 5-HMF oxidation, in agreement with other authors.[24]

However, we have synthesized different mixed oxides with the aim to enhance the selectivity towards FDCA. For sake of clarity, we specify that the terms binary, ternary, quaternary oxides refer to the total number of different elements in the oxide. MO and M_2O are binary oxides, MM'O is a ternary oxide, and so on (IUPAC Nomenclature, 2005). The composition and elemental analyses of mixed oxides used in the present paper are reported in Table S1, while S-BET surface and basic/acid properties are in Table 2, Entries 4-8.

Considered the results obtained with $CuO{\cdot}CeO_2$ discussed above,[20,18b,25] we have investigated the use of MnO_2, that exhibits good ability to activate oxygen[26] and in general behaves as a strong oxidant (E^0 Mn^{4+}/Mn^{2+}=1.23 V), in combination with CeO_2. $MnO_2{\cdot}CeO_2$ was, thus, used in the oxidation of 5-HMF and the correlation between the calcination temperature of the catalyst and the selectivity towards FDCA was studied, together with other parameters such as oxygen pressure and temperature.

The calcination of $MnO_2{\cdot}CeO_2$ was carried out at three different temperatures: 723 K, 825 K and 923 K and the solids tested in the oxidation of 5-HMF (Figure S1). The reaction mixtures were usually analysed when the plateau in the

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conversion was reached (3 h). As Fig. S1 shows, FDCA yield is maximized when the solid calcined at 825 K is used as catalyst.

It is worth to note that good selectivity towards FFCA (63%) was reached using the catalyst calcined at 923 K with a low yield of undesired products such as FA. Increasing the reaction time to 24 h FFCA was not converted into FDCA: rather, the formation of the products derived from the degradation of FFCA, such as FA as well as humins, was enhanced instead.

The influence of the reaction temperature was evaluated during the first hour of reaction, in order to evaluate the product distribution. Experiments at 383, 403, and 423 K have been performed (Figure S2), using $(MnO_2\cdot CeO_2)_{825K}$ as catalyst.

In general, the conversion was increased with the reaction temperature. High temperatures, 423 K, anyway enhance the formation of FA in agreement with the observations reported by other authors[27] who have set at 423 K the minimum temperature for catalysing the transformation of 5-HMF towards LA and FA. The fact that at such temperature the selectivity of HMFCA was higher than the selectivity towards DFF, suggests that there is a change of the pathway of the reaction (Fig. 1) as the aldehyde moiety is preferentially oxidized with respect to the alcoholic.

As the ratio mmol of O_2/mmol of substrate increases as the P_{O2} is increased, we have tested the effect that the increased O_2 concentration at different temperatures has on the selectivity towards FDCA. The results are presented in Figure S3. The highest yield of FDCA was obtained working at 2 MPa of pressure and 403 K. When 3 MPa of pressure was used, lower selectivity towards FDCA was obtained as well as was enhanced the production of FA, usually detected under harsh conditions. These observations agree with other authors that suggest that a high pressure is not necessary to reach high yields of FDCA.[12a,28] Therefore, high oxygen concentration and high temperature are not recommended because their combined use drives to the ring-cleavage producing FA and LA.

The yield of FDCA was increased as the concentration of 5-HMF was decreased, (Table 2, Entries 1 - 3). There were no changes in the reaction pathway, since DFF and FFCA were formed and HMFCA was not detected (Fig. 1).

As reported above, the oxidation of 5-HMF to FDCA is usually performed with the assistance of external bases.[29] *Basic conditions* on the reaction site can even be generated by choosing the catalysts with the correct ratio n_b/n_a [20,18b], avoiding external bases, minimizing waste production and, altogether, performing a more sustainable process.

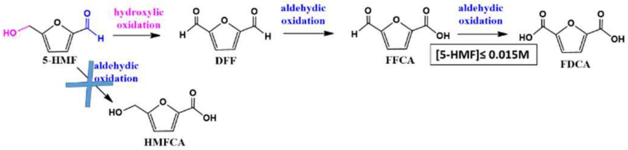

Figure 1. Oxidation of 5-HMF towards FDCA: a plausible pathway. HMFCA is not observed

The mixed oxides have quite different properties than the parent single oxides (see Table 2, respectively). Moreover, the number of both the acidic and basic sites varies as the calcination temperature changes (Figure S4): precisely, the basicity decreases as the calcination temperature increases. A higher selectivity towards FA was observed using the most acidic catalysts $(MnO_2\cdot CeO_2)_{923K}$.

Taking all these informations into consideration, and our knowledge of the oxidation of 5-HMF,[20,18,30] we decided that the best option was to use the mixed oxide based on $MnO_2\cdot CeO_2$ and modulate its properties (activity and selectivity) by using a third oxide.

CuO was selected as the third oxide because the relevant mixed oxides singularly built with CeO_2 present high selectivity towards FFCA (90%):[25] the inclusion of MnO_2 would enhance the oxidation power so to obtain FDCA in good yield. In fact, in the same reaction conditions optimized for the production of FFCA using $MnO_2\cdot CeO_2$ as catalyst, the quaternary oxide $CuO\cdot MnO_2\cdot CeO_2$, gave FDCA with a selectivity of 70.8% (Table 3, Entry 1), and residual FFCA (26.7%).

With respect to pure MnO_2, leaching of Mn was not detected. A study was, thus, performed in order to observe the product distribution with time: Figure S5 shows that only a moderate increase in the production of FDCA was observed for a long reaction time (40 h).

Table 3. Study on the oxidation of 5-HMF using CuO-MnO2-CeO2 mixed oxide as catalyst.

Entry	Solid	t (h)	PO_2	Conv.(%)	Selectivity (mol %)					
					DFF	HMFCA	FFCA	FDCA	FA	LA
1	$CuO\cdot MnO_2\cdot CeO_2$	12	2	97.4	2.4	0	26.7	70.8	0	0
2	Added fresh $CuO\cdot MnO_2\cdot CeO_2$	3	2	99	0	0	0	98.7	0	0
3	Calcined $CuO\cdot MnO_2\cdot CeO_2$	4	2	99	0	0	0	98.6	0	0

Reaction conditions: $[5\text{-HMF}]_i$=0.015 M, 0.05 g of catalyst, 7 mL of water, temperature=403K. * Temperature=383 K

To shade light on the reasons of such limitation, we have performed two experiments: (i) in the first one, after 12h of reaction, the liquid phase was isolated from the catalyst, then fresh catalyst was added to such solution (Entry 2, Table 3) and the reaction continued; (ii) in the second, after filtered off, the catalyst was calcined for 3 h at 823 K and added again to the original solution (Entry 3) and the reaction continued. In both experiments, the catalyst was able to completely oxidize FFCA into FDCA (99%) in short period of time, 3 and 4 h respectively. This fact means that after 12 h the rate of the transformation of FFCA into FDCA is almost stopped by some reversible passivation events, that are removed by calcination. IR and solid state NMR of the solid catalysts isolated after 12 h of reaction did exclude that the deactivation might be due to deposit of humins[31] or other organics.[20] However, in order to shade light on the events which deactivate the catalyst, it was

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characterized before and after a catalytic run, by measuring several properties.

The ratio n_b/n_a and the value of S-BET surface do not change significantly during catalysis. A variation < 1-3% was measured: catalysts were stable and leaching of metal oxides was not observed by using EDX or FLAAS. Therefore, such properties are stable and do not influence the catalytic activity.

However, the XPS and XRD were taken before and after reaction: after a catalytic run, the reaction was stopped, the quaternary catalyst was separated by filtration, washed three times with 5 mL of water, dried and analysed. The recovered catalyst was, then, calcinated at 823 K and re-used. The procedure was repeated twelve times. Figure 2 shows the trend over the first 5 runs: such trend remained unchanged for additional seven runs. No significant loss in the activity (blue bars in Figure 2 give the conversion of 5-HMF in each run) or selectivity (brown bars for FFCA and grey bars for FDCA) was observed after even 12 runs. The surface of the ternary $MnO_2{\cdot}CeO_2$ and quaternary $CuO{\cdot}MnO_2{\cdot}CeO_2$ mixed oxide were, thus, investigated by XPS. For $MnO_2{\cdot}CeO_2$, Ce3d and Mn2p3/2 spectra before and after reaction are presented in Figure S6 a,b, respectively. The relevant surface composition is summarized in Table S3. According to the XPS spectra, CeO_2 consists of only cerium(IV)oxide (Figure S7a) and similarly, the Mn spectrum (Figure S7b) shows only Mn in the oxidation state +4.

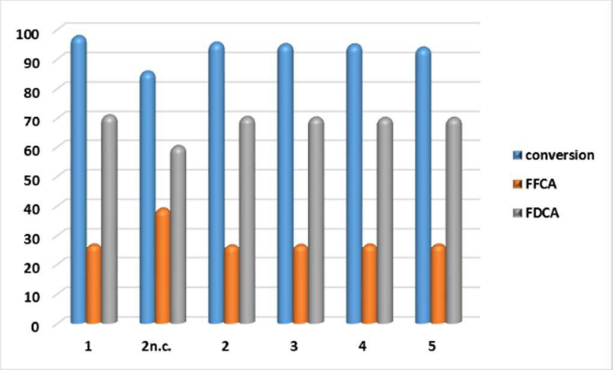

Figure 2. Recyclability of $CuO{\cdot}MnO_2{\cdot}CeO_2$ in the oxidation of 5-HMF towards FDCA and FFCA: the blue bars give the conversion of 5-HMF (read on the left Y-axis) and the brown and grey bars give the selectivity towards FFCA and FDCA, respectively.

Nevertheless, the mixed oxide presents slight variations of the surface composition after reaction: the $MnO_2{\cdot}CeO_2$ corrected area ratio before and after reaction changed from 1.3 to 1.7, each element in the oxidation state +4.

The XRD patterns of the catalyst before and after reaction (Figure S7) show the presence of the crystalline phase attributed to CeO_2 and of peaks with low intensity due to MnO_2 phase (Figure S8). Phase(s) identification was achieved by the qualitative phase analysis computer software *QUALX2.0*.[33] After reaction, the patterns are perfectly overlapping, that means that the catalyst is robust and there were no changes in the structure. (Figure S7) The same analyses were carried out on the quaternary mixed oxide $CuO{\cdot}MnO_2{\cdot}CeO_2$. The XPS, Ce3d, Mn2p3/2 and Cu2p3/2 spectra before and after reaction are shown in Figure S9a, b, c. As shown in Table S3, the surface atomic composition after reaction presented variations of the content of the three metals, which changed from 3.2:1.1:1 (Mn:Ce:Cu) to 3.2:2.8:1, evidencing a cerium surface enrichment, with a Ce migration from the bulk to the surface of the solid. The oxidation state did not present variation for Mn and Ce, while 30% of Cu(0) was found on the surface: this can explain the reduced activity in the oxidation after 12 h reaction. After calcination, Cu(0) is oxidized back to CuO and the activity of the catalyst is fully restored.

XRD analysis (Figure S10) of the quaternary catalyst before reaction and after reaction, show that the two patterns are perfectly overlapping.

In order to identify the role of the oxides, we have carried out a test in which 5-HMF was treated with the quaternary oxide in absence of oxygen. 5-HMF oxidation products were observed even if at the level of a few units per cent. The XPS analysis of the sample before and after reaction showed that CuO was reduced to Cu, justifying thus the presence of Cu(0) in the normal catalytic runs, with very minor presence of reduced Ce(IV) and Mn(IV). The reaction mechanism will be matter of further investigation. For now, it seems that CuO is the oxidant and it is reoxidized by O_2 with the mediation of other oxides (MnO_2 or CeO_2). It is worth to note that, as said above, there is no evident release of metals in solution during the catalytic runs. Anyway, to eliminate doubts, we have tested single components dissolved in water in the form of hydroxides. Their performance was really almost zero and neither FDCA nor other oxidation products of 5-HMF were formed. However, we conclude that the real catalyst is the heterogeneous quaternary oxide.

Finally, increasing the content of CuO in the catalyst to $1.5CuO\text{-}MnO_2\text{-}CeO_2$, it was possible to carry out the oxidation of 5-HMF into FDCA (99% conversion with 99 % selectivity towards FDCA) in the same conditions reported in Table 4. The catalyst is stable, fully recoverable and is reusable in other runs after calcination. XPS shows only very limited CuO reduction to Cu(0) with respect to the total amount of copper oxide.

Conclusions

As we have already shown, 5-HMF is catalytically converted in water using oxygen as oxidant affording FDCA (70.1 to 99%) according to the reaction conditions and the catalyst used. The quaternary mixed oxide of formula $CuO{\cdot}MnO_2{\cdot}CeO_2$ is able to convert 5-HMF into FDCA with high yield and selectivity, in aqueous phase under base-free conditions with oxygen as oxidant. Both acidic and basic sites on the surface of the catalysts play an important role to enhance the yield/productivity of FDCA. 5-HMF oxidation proceeds via DFF and FFCA formation rather than HMFCA, to form FDCA. Reaction parameters such as temperature, oxygen pressure and amount of catalysts were investigated. The catalysts showed high stability during twelve runs and were studied for

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the surface by XPS and for the bulk by XRD before and after reaction. The quaternary $CuO{\cdot}MnO_2{\cdot}CeO_2$ oxide is able to convert 5-HMF into FDCA with 71 % yield (plus FFCA 27% and DFF 2.4%, precursors of FDCA) and a transient deactivation due to the reduction of Cu(II) to Cu(0), not leached in solution. Calcination of the used catalyst at 823 K recovered the activity, so that FFCA was further oxidized to FDCA with an overall yield of the latter set at *ca*. 99%. The quaternary mixed oxide revealed to be an efficient, recoverable and reusable cheap catalyst made of abundant metals for the efficient oxidation of 5-HMF into FDCA in water using O_2 as oxidant, and the process environmentally benign and sustainable. With respect to Pt/C-Bi, the quaternary catalyst described in this paper results to be kinetically slower, but shows the advantage of not using external bases nor precious metals and being fully recoverable and reusable.

Conflicts of interest

"There are no conflicts to declare".

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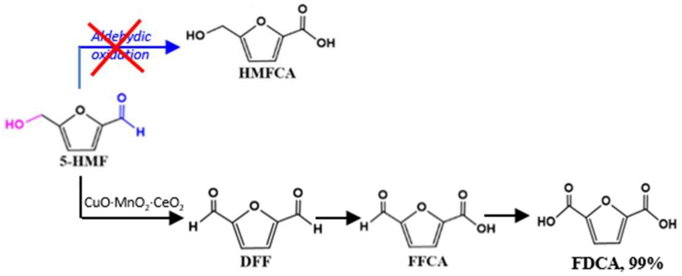
The selective oxidation of 5-HMF towards 2,5-furandicarboxylic acid (FDCA) has been achieved with 99% yield in water, using oxygen as oxidant over $CuO^{\cdot}MnO_2^{\cdot}CeO_2$ mixed oxides.



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