Selective Oxidation of 5-(Hydroxymethyl)furfural to DFF Using Water as Solvent and Oxygen as Oxidant with Earth-Crust-Abundant Mixed Oxides

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ABSTRACT: 5-Hydroxymethylfurfural (5-HMF) can be considered a prominent building block: because of the presence of the alcohol and aldehyde moieties, it can be used to generate useful molecules as chemicals of industrial interest with high added value, monomers for polymers, and even fuels. This article shows how building up mixed oxides of different complexities and properties may drive the selectivity toward one of the possible products generated from 5-HMF. In particular, mixed oxides based on cerium and other metals abundant on the earth-crust perform the selective oxidation of 5-HMF to 2,5-diformylfuran (94%), using oxygen as oxidant and water as solvent. The roles of the reaction conditions (temperature, reaction time, oxygen pressure, concentration of the substrate), the chemical composition, the acidic/basic properties, and redox properties of the catalysts are discussed.

1. INTRODUCTION

About 90% of synthetic organic materials used in everyday life are derived from oil. Replacement of fossil carbon with second-generation biomass (cellulose) is a key factor in boosting the sustainability of the chemical industry, as it avoids fossil-CO₂ emission and provides a diversity of raw materials. The challenging task is to develop new catalysts that may selectively convert cellulose-derived polyols into useful products. Particular attention has been received by 5-hydroxymethylfurfural (5-HMF) (Figure 1), used as the source of several products, each with peculiar properties. We have recently developed a process for the production of pure 5-HMF used for the selective synthesis of each of the products shown in Figure 1. Among the products of oxidation of the pending arms of 5-HMF, particular attention has been received by FDCA (1,5-furandicarboxylic acid) as it has been used as co-monomer with etheneglycol for the production of poly(ethenefuranoate) as substitute for poly-ethene terephthalate originated from oil.

2,5-diformylfuran (DFF) (Figure 1) is another platform molecule, from which fine chemicals and drugs can be derived. Usually, DFF is synthesized in organic solvents, because of its scarce stability in water in the presence of bases, using precious (gold) or expensive metals, such as ruthenium. Of the selectivity, 64.2% was achieved with 30.2% conversion, using as catalyst Cu/Cr/V-doped MnO₂ in the presence of oxygen as oxidant, carrying out the synthesis in organic solvents. Even organic co-catalysts, such as N-hydroxyphtalimide, have been used with metal systems to produce DFF starting from 5-HMF in organic solvents. Recently, double-layered hydroxides of formula Mn₀.₇₀Cu₀.₀₅Al₀.₂₅OH, with not fully disclosed structural features, have been reported to efficiently produce DFF in water.

We have studied the selective oxidation of 5-HMF using oxygen and water under nondrastic conditions and developed specialized catalysts for the various products. Formyl-furan-carboxylic acid (FFCA) was produced using CuO and CeO₂ as catalysts. The selective oxidation to HMFCA (2-hydroxymethyl-furan-5-carboxylic acid) was achieved using the mixed

Figure 1. Products of side-chain oxidation of 5-HMF.
oxide MgO-CeO₂₁₅. The selective formation of FDCA was achieved using quaternary mixed oxides made of CuO–MnO₂ and CeO₂.₁₆

In this article, the selective aerobic oxidation of 5-HMF to DFF will be discussed, putting emphasis on how combining binary oxides, each not quite selective toward DFF, it is possible to build up a catalytic material which produces DFF with over 90% selectivity and almost total conversion of 5-HMF in water. Noteworthily, in the literature, promoting the selective formation of FDCA was as weak (because of the protons of the surface OH-groups) and medium and strong properties. Analogously, acidity is classified on the surface; the desorption occurs in the range of 290–430 K;

(ii) Medium basic attributed to the M=O moieties; the desorption occurs in the range of 430–670 K;

(iii) Strong basic because of isolated oxide species; the desorption occurs above 670 K.

As the weak acid/basic sites do not have an active role in catalysis, in this work we have considered only basic sites with medium and strong properties. Analogously, acidity is classified as weak (because of the protons of the surface OH-functionalities) and strong acidity (Lewis acid metals, M⁺).₁₈

Table 2 shows that the single oxides have different acidic/basic properties. In our previous studies, we have correlated the “ratio of strong basic/acidic sites (n_b/n_a)” to the activity of the catalysts used and, in part, for tuning their activity and selectivity, supposed that the mixed oxides had the correct potential for the targeted oxidation.₁₄–₁₆ Looking at Table 2, it is clear that depending on the single oxides used different products are obtained: CeO₂ affords mainly FFCA, MnO₂ affords FDCA as the majoritary product, but, as said earlier has the drawback that it dissolves in water under the reaction conditions. MgO is not able to produce any selective oxidation of the arms of 5-HMF and only a degradation products are formed. LA is levulinic acid.

2. RESULTS AND DISCUSSION

2.1. Single Oxides: Assessment of the Catalytic Activity. Binary oxides of available elements on the Earth crust, such as MgO, MnO₂, and CeO₂, have been used. Their choice was dictated by our previous experience.₁⁴–₁₆ In a first stage of the work, the catalytic activity of the single oxides was estimated. Table 1 shows the activity of various catalysts (single oxides) used in the oxidation of 5-HMF in the presence of O₂. We have already reported₁⁴ that by using CeO₂ (Table 1, entry 1) the main oxidation product is FFCA. MnO₂, a stronger oxidant, gives FDCA as the main (75.5%) oxidation product, accompanied by 23.5% of FFCA and a minute amount of levulinic acid (LA) (Table 1, entry 2). MgO is not a reox catalyst but is used in mixed oxides for tuning their basic properties: by using MgO alone, formic acid (FA) and humins were detected because of thermal 5-HMF decomposition (Table 1, entry 3).

MnO₂ has the drawback of its water solubility that makes it not appropriate as a heterogeneous catalyst: EDX (Energy Dispersive X-rays) measurements did show that 75% of the original solid was dissolved in water.

2.2. Characterization of the Single Oxides. Table 2, entries 1–3, reports the Brunauer, Emmett, and Teller (BET) surface area and the ratio between (weak and strong) acid and (weak and strong) basic sites for single oxides. The latter were calculated from the NH₃/CO₂ thermo-desorption curves. The strength of different basic/acidic sites is categorized as:₁⁷

(i) weakly basic because of the presence of hydroxyl groups on the surface; the desorption occurs in the range of 290–430 K;

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The BET surface area (Table 2, entries 1–3) varies in the order MgO < MnO₂ < CeO₂ and the trend is not correlated to the specific activity of the catalysts, as also shown by other authors.¹⁹

The H₂-Temperature Programmed Reduction (TPR) (Figure 3) shows a profile associated to the different redox property of the single oxides: CeO₂ shows a reduction peak at a much higher temperature than MnO₂. A low reduction temperature implies a higher O-transfer potential: MnO₂ is a better oxidant than CeO₂. MgO does not show any reduction peak in a reasonable temperature range, as expected. Table 1 shows that single oxides do not promote high (>90%) selectivity toward any of the oxidation products of 5-HMF. However, we have synthesized various mixed oxides so as to have stable heterogeneous catalysts capable of enhancing the selectivity toward DFF.

2.3. Evaluation of the Activity of the Ternary Mixed Oxides. To avoid misunderstandings, it is worth to emphasize that the IUPAC Nomenclature (2005) was used for the definition of binary, ternary, or quaternary oxide. Therefore, considering the number of different elements, an oxide of the type MO and M₂O is named binary, M₃O’ is a ternary oxide, and so on.

Table 3 shows the analytical data (theoretical and experimental) of the mixed oxides used. The BET surface area and the strength of the acid and base sites are shown in Table 2 (entries 4–7). As we have already reported, when CuO-CeO₂ is used as catalyst¹⁴ 5-HMF is converted with high selectivity (90%) to produce FFCA at 99% conversion, whereas MgO-CeO₂¹⁵ shows a high selectivity toward HMFCO (97%) and the quaternary oxide CuO-MnO₂-CeO₂ affords FDCA with >90% selectivity at a total conversion of 5-HMF.¹⁶

Considering the above evidence, we have investigated first the behavior of MnO₂-CeO₂, and then of MgO-MnO₂-CeO₂. The activity and selectivity of the used catalysts were evaluated considering the influence of different parameters such as the dependence on the oxygen pressure, the temperature, and the initial concentration of 5-HMF. Furthermore, the effect of the calcination temperature was also evaluated.

2.4. Influence of Calcination Temperature on the Activity of MnO₂-CeO₂. MnO₂-CeO₂ was calcined at different temperatures such as 723, 823, and 923 K and then was used as catalyst in the oxidation of 5-HMF (Figure 4). The analyses of the liquid phase were carried out after 3 h (plateau). As Figure 4 shows, the DFF yield was increased by 10 times with respect to single binary oxides (see Table 1) and was maximized with the solid calcined at 825 K. As reported in Figure 5, it is clear that the calcination temperature affects the ratio of acid/basic sites and the increase of temperature favors the acidity. As a matter of fact, most acidic catalysts (Mn/ Ce)₉₂₃₋₉₂₅ produce FA.²⁰ Considering the value of the nₐ/nₐ of MnO₂-CeO₂, we decided to modulate its properties by adding a basic oxide to it in order to increase the ratio nₐ/nₐ and try to promote the oxidation of the alcoholic functionality of 5-HMF. MgO was selected as the third oxide.

2.5. Evaluation of the Activity of the Quaternary Mixed Oxide MgO-MnO₂-CeO₂. Table 4 (entries 1 and 2)
shows the results relevant to the use of a quaternary mixed oxide in catalysis. As a comparison, we report the data relevant to the quaternary oxide CuO-MnO₂-CeO₂. The MgO-based quaternary oxide MgO-MnO₂-CeO₂ afforded 94.9% selectivity toward DFF at a conversion close to 70% (entry 1) after 6 h of reaction and 98.8% conversion at 95.2% selectivity after 10 h. The CuO-based quaternary oxide produced mainly FDCA.

Table 4 clearly shows the effect of a third oxide on the couple MnO₂-CeO₂; whereas the basic oxide MgO addresses the reaction toward the oxidation of the −CH₂OH moiety that is converted into the −CHO moiety, such effect was expected as the basic conditions to favor the deprotonation of the alcoholic moiety and its oxidation; the addition of CuO, an oxidant, promotes the complete oxidation of both pending arms of 5-HMF into the carboxylic group −CO₂H. It worth to emphasize that a maximum temperature of 383 K was used in the case of the MgO-MnO₂-CeO₂ (see the following paragraph for explanation). Table 4 shows the product distribution at two different times of reaction. Noteworthily, the further oxidation of the formyl moieties was not observed with the MgO-MnO₂-CeO₂ quaternary catalyst even at longer reaction times.

### 2.6. Characterization of the Quaternary Mixed Oxide MgO-MnO₂-CeO₂ before and after Catalysis.

We have investigated how the properties of the quaternary oxide are affected during catalysis. At the end of the catalytic test, the catalyst was separated by filtration from the reaction mixture and washed with distilled water (2 × 3 mL) and dried in vacuo at 370 K. The ratio nₚ/nₓ and the value of BET are not affected (variation of 1%) by the use in catalysis. The recovered catalysts were analyzed by EDX and leaching of metals was not observed.

H₂-TPR analysis of the mixed oxides was performed to understand how the properties of the starting oxides were modified in the mixed oxides. It is interesting to note that, considering the quaternary mixed oxide MgO-MnO₂-CeO₂, one can find that even if MgO does not present a reduction peak in a reasonable temperature range, it influences the redox properties of the ternary MnO₂-CeO₂ oxide. The profile (Figure 6) shows that the two reduction peaks for Mn/Ce are shifted and collapse into one: most probably, the quaternary oxide shows higher oxidizing power comparing with binary and ternary oxides with a boosted oxidation of 5-HMF toward DFF. The basic properties of MgO play a key role in this catalytic material.

#### 2.7. Recyclability of the Catalysts.

In order to clarify whether catalysis occurred on the solid catalyst or in solution, the reaction solution was filtered and the liquid phase characterized for its composition. Metals were not detected if not at a sub-trace concentration (ppm level). Such solution was anyway used in a separate experiment of oxidation in the same conditions used with the solid catalysts. No oxidation of 5-HMF was observed. If the quaternary catalyst was added, 5-HMF was oxidized. This clarifies that catalysis is really heterogeneous. We have also investigated how the catalytic run influences the properties of the catalyst by using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) technique and we have carried out measures before and after the catalytic test. As a general procedure, after each step, the autoclave was cooled down and opened to recover the quaternary catalyst. This latter was filtered, washed with distilled water (3 × 5 mL), dried in vacuo at 323 K, and analyzed by XPS and XRD. Then, they were calcined at 823 K and re-used with fresh samples of the substrate. The recovery process was carried out several times. Figure 7 illustrates the test performed using MgO-MnO₂-CeO₂ that was, thus, obtained in almost quantitative yield with respect to the starting material.

A decrease of the activity of the catalyst was observed when the tests were performed using Mg/Mn/Ce at 403 K. After the third run, the conversion (blue bar) was heavily decreased, whereas DFF selectivity remained high (purple bar). The EDX analysis after the run revealed leaching of Mg as Mg(OH)₂, and the increase of the ratio Ce/Mg from 5.3 to 6.8.

It is worth to note that when the catalytic test was performed at 383 K, the catalyst maintained its activity, stability, and selectivity for a long time as leaching was prevented. In fact, the recovered catalyst when re-used in the oxidation of 5-HMF in two more runs gave the following results: conversion: 99, 98.8%; selectivity: 95; 96.1%, respectively, for run 2 and run 3.

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**Table 4. Use of Quaternary Oxides M/Mn/Ce Oxide (M = Cu, Mg) as Catalysts**

| entry | solid          | t (h) | PO₂ | conv.(%) | selectivity (mol %) | DFF | HMPCA | FFCA | FDCA | FA | LA |
|-------|----------------|-------|-----|----------|---------------------|-----|-------|------|------|----|----|
| 1     | MgO-MnO₂-CeO₂  | 6     | 2   | 69.7     | 94.9                | 1.5 | 0     | 0    | 0    | 1.5| 1.5|
| 2     | MgO-MnO₂-CeO₂  | 10    | 2   | 98.8     | 95.2                | 0.8 | 0     | 0    | 0    | 1.85| 2.1|
| 3     | CuO-MnO₂-CeO₂  | 4     | 2   | 79.0     | 0                   | 0   | 0     | 98.6 | 0    | 0  | 0  |

*a Reaction conditions: [5-HMF]ᵢ = 0.015 M, 0.05 g of catalyst, 7 mL of water. *b Temperature = 383 K. *c Temperature = 403 K.

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**Figure 6.** H₂-TPR profile of (a) MnO₂, MnO₂-CeO₂, CeO₂; (b) MnO₂-CeO₂, MgO-MnO₂-CeO₂.
3. CONCLUSIONS

In this article, we have shown that 5-HMF can be converted into DFF, a platform molecule derived from biomass, with high yield (up to 99%) and selectivity (95%) in aqueous phase under external base-free conditions with oxygen as oxidant and in the presence of the quaternary mixed oxide of formula MgO-MnO₂·CeO₂. The catalyst at 403 K underwent leaching after the third run. At 383, the stability was much increased and the catalyst performed well for several runs. Catalysis occurs on the solid catalyst and best operative conditions are represented by [5-HMF]₀ = 0.015 M; P₀ = 2 MPa; T = 383 K. The use of the basic component of the catalyst has a key role in the reaction path and selectivity of the process. In fact, it favors the deprotonation of the alcoholic functionality of 5-HMF, improving the H-transfer from such group with respect to the formyl group, avoiding the formation of carboxylic moiety.

It is worth to point out that the conversion of bio-based 5-HMF into DFF with high yields in the absence of a base using heterogeneous systems is an example of a sustainable and ecofriendly process.

4. MATERIALS AND METHODS

All reagents were ACS grade Sigma-Aldrich products. 5-HMF was obtained as described in ref 5.

A high-energy milling (HEM) apparatus Pulverisette 7 Fritsch was used to prepare the catalysts.

To measure the 5-HMF conversion kinetics at a fixed temperature, a 50 mL stainless-steel reactor equipped with a valve to pick up the sample at a fixed time and an electrical heating jacket was used.

The conversion of 5-HMF and formation of its derivatives were monitored by high-performance liquid chromatography (HPLC) (Jasco PU-2089 PLUS) connected to a Refractive Index (RI) detector. The following HPLC analysis conditions were used: Phenomenex Rezex RHM Monosaccharide H⁺ Index (RI) detector. The following HPLC analysis conditions were used: Phenomenex Rezex RHM Monosaccharide H⁺ Index (RI) detector. The following HPLC analysis conditions were used: Phenomenex Rezex RHM Monosaccharide H⁺ Index (RI) detector. The following HPLC analysis conditions were used: Phenomenex Rezex RHM Monosaccharide H⁺ Index (RI) detector. The following HPLC analysis conditions were used: Phenomenex Rezex RHM Monosaccharide H⁺ Index (RI) detector.

Gas chromatography analyses were carried out with Thermo Scientific equipment by using the following conditions: 323 K (2 min)—7°/min → 393 K (8 min)—15°/min → 403 (10 min).

Quantitative oxides analyses were performed by using a Shimadzu EDX-720/800 HS (5–50 kV Rh target X-ray generator, Si (Li) detecting system). The analyses were carried out at room temperature and N₂ liquid was used to cool the detector.

A scanning microprobe PHI 5000 VersaProbe II (Physical Electronics, Chanhassen, MN) connected with a monochromatized Al Kα X-ray radiation source was used to perform XPS analyses. The registered high-resolution spectra (Fixed Analyser Transmission (FAT) mode, pass energy 29.35 eV) were processed by using the MultiPak software package (version 9.6.1.7).

The measurement of the specific surface area was performed with BET technique by using a Micromeritics Chemisorb 2750 equipment. NH₃ and CO₂ were used as probe gas with 100 mg of catalyst (pretreated under 30 mL min⁻¹ N₂ flow at 823 K) to analyze the acid and basic sites, respectively. In all the experiments, He was used as carrier gas (30 mL min⁻¹).

The structure of the catalysts was studied recording powder X-ray diffraction patterns at room temperature using a Bruker D8-DISCOVER [Bruker AXS, Karlsruhe, Germany] powder diffractometer connected with a Göbel Mirror for Cu Kα radiation (λ_Kα1 = 1.54056 Å and λ_Kα2 = 1.54439 Å). The analysis conditions were 40 kV and 50 mA; data were collected in the 2θ range between 10° and 120°, with a 0.05° step size and a counting time of 1 s per step, with 2θ/ω scan type.

4.1. Catalyst Preparation.

4.1.1. Synthesis of MnO₂·CeO₂·(NH₄)₂·Ce(NO₃)₆. An equivalent amount of (NH₄)₂·Ce(NO₃)₆ (1 mmol; 0.54 g) and 0.08 g of MnO₂ (1 mmol) were placed in agate baskets and pulverized in the planetary mill using the following programme: 790 rpm × 15 min with a 1 min break for a total of 1 h and repetition inverting the rotation sense. The black collected powder was calcined for 3 h at 723–923 K. The solid was then cooled down into a desiccator and transferred into a test tube and preserved under N₂ atmosphere to avoid any kind of decomposition of the catalyst prior to its use. The data for the elemental analysis carried out by EDX are shown in Table 3.

4.1.2. Synthesis of MgO-MnO₂·CeO₂. An equivalent amount of (NH₄)₂·Ce(NO₃)₆ (1 mmol; 0.54 g), manganese(IV) oxide (1 mmol; 0.08 g), and the nitrate of the desired metal (1 mmol) were mixed and pulverized using HEM, calcined, and stored as described above (a). The data for the elemental analysis carried out by EDX are shown in Table 3.

4.2. Catalytic Tests and Product Analysis.

A solution of 5-HMF (1 mmol, 0.126 g) in deionized water (7 mL) was prepared in a glass reactor, where 0.05 g of the catalyst under study and a magnetic stirrer were also added. The glass reactor was placed into a stainless-steel autoclave that was closed, purged three times with O₂, charged at the proper O₂ pressure, and heated to the specific reaction temperature (see the Results and Discussion section). The reaction was followed by sampling the reaction mixture at fixed intervals of time and monitoring, by HPLC, the disappearance of 5-HMF. In this way, the reaction could be stopped when the concentration of 5-HMF remained constant or even approached zero. At the end of the reaction, the autoclave was opened, the reaction mixture recovered and extracted with ethyl acetate (EtOAc) (3 × 7 mL). This operation was useful to recover the formed DFF which is not very soluble in water and can precipitate. The EtOAc solutions were collected, washed with water to extract 5-HMF dissolved into it, desiccated with Na₂SO₄, filtered, and analyzed by GC. Evaporation in vacuum of EtOAc gave the pure DFF (98% yield).
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**Notes**
The authors declare no competing financial interest.

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