Selective oxidation of 5-hydroxymethyl furfural over non-precious metal heterogeneous catalysts

Florentina Neaţu [a,*], Roxana Simona Marin [a], Mihaela Florea [a], Nicoleta Petrea [b], Octavian Dumitru Pavel [a], Vasile I. Pârvulescu [a,*]

[a] University of Bucharest, Faculty of Chemistry, Department of Chemical Technology and Catalysis, 4-12 Regina Elisabeta Bvd., Bucharest 030016, Romania
[b] Scientific Research Centre for CBRN Defense and Ecology, 225 Oltenitei Sos., 041309 Bucharest, Romania

ARTICLE INFO

ABSTRACT

An alternative synthesis of 2,5-furandicarboxylic acid (FDCA) was carried out by oxidation of 5-hydroxy-2-methyl furfural (HMF) in aqueous medium. The reaction occurred in presence of non-precious metal (Mn_xFe_y) mixed oxide catalyst. The effect of various reaction parameters such as nature and amount of base, reaction temperature, oxygen pressure, catalyst composition were investigated in order to quantitatively produce FDCA. The catalytic behavior of the mixed oxide catalyst was assigned to an optimal Mn/Fe ratio of 3/1, where a mixture of Mn(III) and Mn(IV) coexists with a hematite phase. The synergetic cooperation of these phases allowed the efficient oxidation of FFCA to FDCA. The humins species formed by HMF degradation exhibited a negative effect over the catalytic activity of Mn/Fe mixed oxide, while the chlorine resulted after the pH modification had no influence upon the catalytic oxidation.

1. Introduction

Depletion of fossil resources has generated serious concerns during the past decade. Currently, production of both energy and chemicals requires alternative resources and a severe environmental control [1]. A potential solution could be the use of renewable resources. Since renewable resources like biomass already contain oxygen, such a strategy is mostly feasible for the production of oxygen-containing compounds [2].

Following this strategy, alternative to polyethylene terephthalate (PET) can be economically produced from the oxidation of 5-Hydroxymethyl-2-furfural (HMF). HMF represents an important, versatile and available primary renewable platform molecule that is structurally found into numerous pharmaceuticals, antifungal agents, as well as polymers, whose synthesis is attempted starting from carbohydrates such as fructose, glucose, cellulose etc [3–9]. Then, 2,5-Furandicarboxylic acid (FDCA) is a promising biomass-derived chemical building block with a great market potential. It is considered one of the top added-value chemicals among biomass [10] merely because it may conveniently replace terephthalic acid in PET [11] manufacture. The classic synthesis of FDCA from HMF usually involves high pressure and temperature, metal salts and organic solvents [12–16] which render the process to be quite expensive and polluting. Therefore, a new greener route for the synthesis of FDCA may be designed in the presence of versatile heterogeneous catalysts.

The literature survey for the oxidation of HMF to FDCA indicated that this reaction has been performed using stoichiometric amounts of oxidants and expensive catalytic systems containing noble metals such as Pt [17–22], Pd [23–26], Au [27–32], Ru [33], or their alloys [34–41]. In addition, the presence of a base is crucial in order to facilitate the desorption of the resulted acid from the catalytic surface. However, the presence of the base can lead to a gradual degradation of HMF [32,42–44]. Other reports claim a high selectivity to FDCA without the addition of any base, [45,46] when TBHP is used as oxidizing agent and $CuCl_2$ as catalyst (selectivity of 48% after 48 h [46]).

On the other hand, manganese oxides including bulk and supported MnO_2, Mn_2O_3 and Mn_3O_4 on silica, alumina, titania and zirconia were reported as efficient cheaper alternatives in environmental oxidation catalysis. These oxides are known to exhibit high activity in hydrocarbon and VOC catalytic combustion, oxidation of HMF to DFF [47], as well as other oxidation reactions [48,49]. Their catalytic behavior is related to both redox capabilities and acid-base properties, and as it resulted from the work of Liu et al. [47] the promotion of the HMF oxidation depends on the oxidation state of manganese and its surroundings.
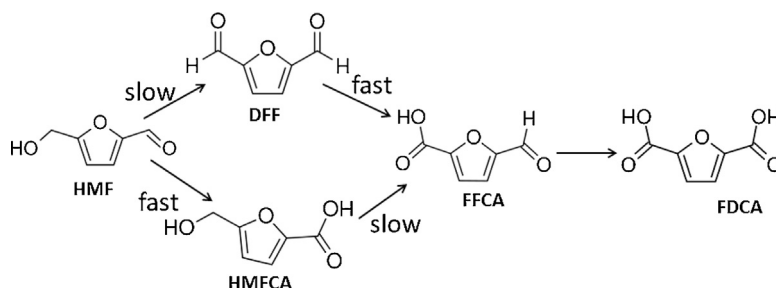
Scheme 1. Reaction pathways in oxidation of HMF to FDCA (DFF: 2-diformyl furan; FFCA: 5-formyl-2-furancarboxylic acid; HMFCA: 5-hydroxymethyl-2-furancarboxylic acid).

Herein, we report an environmentally benign and safe alternative for the synthesis of FDCA (Scheme 1). The oxidation of HMF was carried out under mild aqueous conditions, using Mn/Fe mixed oxides as heterogeneous catalysts.

Mn/Fe mixed oxides in 1:3, 1:1 and 3:1 atomic ratios, respectively, were prepared by co-precipitation method. For comparison purposes, pure Mn and Fe oxides were also prepared following the same procedure. The obtained catalysts were denoted MnX/Fe(1-X), where $X = 0.75, 0.50, 0.25$.

2. Experimental

All reagents were of analytical purity: 5- hydoxymethyl-2-furfural (HMF, Sigma–Aldrich 99%), 5-formyl-2-furancarboxylic acid (FFCA, Sigma–Aldrich), 2,5-furandicarboxylic acid (FDCA, Sigma–Aldrich 97%), diformyl furan (DFF, Sigma–Aldrich 97%), He (purity 5.0, Linde), CO_2 (Linde Romania), NH_3 (Siad Romania), O_2 (purity 5.0, Linde Romania), $Mn(NO_3)_2$ hexahydrate (Sigma–Aldrich), $Al(NO_3)_3$ nonahydrate (Fluka 98%), Fe $(NO_3)_3$ nonahydradate (Sigma–Aldrich $\geq$98%), Fe_2O_3 (Sigma–Aldrich), $Mn(CH_3COO)_2$ tetrahydrate (Fluka $\geq$ 99%).

2.1. Catalysts synthesis

Mn/Fe mixed oxides with molar ratios varying from 1:3, 1:1, and 3:1, respectively, were prepared by co-precipitation method. The preparation procedure started from an aqueous solution of manganese nitrate and iron nitrate, containing the amounts corresponding to the above molar ratios (e.g. for the catalyst Mn0.75/Fe0.25, the calculated amount were 53.7 g (0.3 mol) $Mn(NO_3)_2 \cdot 6H_2O$ and 40.4 g (0.1 mol) $Fe(NO_3)_3 \cdot 9H_2O$) that were pre-mixed. To this solution, at room temperature, an appropriate volume of solutions of NaOH or Na_2CO_3 (1.5 M) were added in order to generate a pH of 9–10. The resulted precipitates were aged overnight at 75 °C under stirring. The final precipitates were filtered, thoroughly washed until pH 7 and dried overnight at 100 °C in an oven. The calcination step has been accomplished at 460 °C for 5 h in air atmosphere. Separately, Mn_2O_3 was prepared by the following method: 2 g of manganese acetate were added into a beaker containing 200 mL of bidistilled water. A sodium hydroxide solution (0.2 M) was added dropwise until a pH 10 was reached. Then the precipitate was aged for 1 h at 80–90 °C and then left overnight at room temperature under stirring. The brown slurry was filtrated and washed with deionized water, then dried overnight at 100 °C and calcined at 460 °C for 5 h in air atmosphere. Fe_2O_3 was prepared mixing solutions of $Fe(NO_3)_3 \cdot 9H_2O$ and NaOH in a molar ratio of 1:3, where that containing sodium hydroxide was dropwise added to that containing iron nitrate under vigorous stirring, until a pH of 9 has been reached. After the addition of NaOH the stirring was continued for another 1 h. The precipitate was then filtered out and washed with deionized water until pH 7, then dried for 16 h at 100 °C, and calcined for 5 h at 460 °C.

2.2. Catalysts characterization

The samples have been investigated using different characterization techniques like powder X-ray diffraction, temperature programmed reduction analysis, XPS, Raman, and textural analysis. The XRD patterns were recorded using a Shimadzu 7000 powder diffractometer which used the Cu Kα radiation (wavelength 1.54184 Å). The patterns were collected in the range 2θ from 5 to 80° in steps of 0.02° 2θ/s. The CO_2-TPD measurements were carried out using AutoChem II 2920 station equipped with a TCD detector working at 250 °C. The samples (30–50 mg), placed in a U-shaped quartz reactor with an inner diameter of 0.5 cm, were pre-treated under He atmosphere at 100 °C for 1 h, and then exposed to a flow of 30 mL min^{-1} CO_2 for 1 h. After that, the sample was purged with a flow of He (100 mL min^{-1}) for 20 min at 20 °C in order to remove the weakly adsorbed species. TPD experiments were then started, with a heating rate of 10 °C min^{-1} until 850 °C. The chemical analysis of the diluted post- reaction mixtures has been performed using a Perkin Elmer ELAN 6000 spectrophotometer with cross-flow nebulizer and argon plasma. To perform the quantification of carbon, nitrogen and hydrogen in the samples, the materials were also characterized by combustion elemental analysis using a Eurovector analyzer from Shimadzu. The textural measurements used the adsorption-desorption isotherms collected with N_2 at −196 °C on a Micromeritics ASAP 2010 sorption analyzer. Before the analysis the catalysts were outgassed at 200 °C in vacuum. The surface areas have been obtained using BET equation. Surface analysis was performed by X-ray photoelectron spectroscopy (XPS) carried out on PHI Quantera equipment with a base pressure in the analysis chamber of 1.3×10^{-12} bar. The X-ray source was monochromatized Al Kα radiation (1486.6 eV) and the overall energy resolution is estimated at 0.6 eV by the full width at half-maximum (FWHM) of the Au4f7/2 photoelectron line (84 eV). The unavoidable charging effect was minimized by using a dual beam (electrons and Ar ions) as neutralizer and the spectra were calibrated using the C1s line (BE = 284.8 eV) of the adsorbed hydrocarbon on the sample surface (C—C or (CH)$_n$ bonding). As this spectrum was recorded at the start and the end of each experiment the energy calibration during experiments was reliable. Raman spectroscopy was performed using a Horiba spectrometer, equipped with a He–Ne ($\lambda = 633$ nm) laser. The spectra were recorded in the 200–4000 cm^{-1} range.

2.3. Catalytic reactions

Catalytic experiments were performed under vigorous stirring in a stainless steel autoclave (HEL Instruments) at temperature (90 °C) following two strategies: (i) in the *one-pot reaction conditions*: 1 mmol of substrate (HMF), 10 mL of MiliQ water, 0.05 g of catalyst and sodium hydroxide in a molar ratio to the substrate of 1:4 were stirred in an autoclave pressurized at 8 bars. (ii) in the *two-steps reaction conditions*: firstly, 1 mmol of substrate (HMF), 10 mL of MiliQ water, and 4 mmoles sodium hydroxide were heated for