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Oxidation of 5-hydroxymethyl furfural to 2,5-diformylfuran in aqueous media over heterogeneous manganese based catalysts

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ABSTRACT

Manganese-copper layered double hydroxides prepared following a conventional procedure were investigated for the selective oxidation of 5-hydroxymethyl-2-furfural into 2,5-diformylfuran. After checking the effect of the different parameters it has been found that a composition corresponding to $Mn_{0.70}Cu_{0.05}Al_{0.25}$, of the catalyst already calcined, led to the highest conversion (90%) and selectivity (87% in DFF). Noteworthy, this has been achieved working under mild aqueous conditions (90 °C and 8 bars O_2). The performances of the catalysts were closely associated to the strength of the basic sites.

1. Introduction

Sustainable valorization of biomass will continue to stay on the future global political agenda, with the scope to ensure a proper development of industry and energy [1–3]. Nowadays, derived from the biomass, the human demand for food and feed constitutes around 80% from the production, while only 20% is used for fuels or industrial purposes [2,3]. Moreover, all analyses predict an increase of both the food/feed and non-food/feed demand. Therefore, tough criteria, parameters and mechanisms are required to ensure that the biomass consumption is not scattered and used in inefficient processes.

5-Hydroxymethyl-2-furfural (HMF) represents an important, versatile and available primary renewable platform molecule derived from biomass that is structurally found into numerous pharmaceuticals, antifungal agents, as well as polymers. 2,5-Diformylfuran (DFF) is one of the oxidation products of HMF which can be used as monomer for the production of fluorescent materials [4] or as a starting compound for the synthesis of drugs, antifungal agents or ligands [5]. Oxidation of HMF can lead to various other products (Scheme 1). Beside the hydroxyl, HMF contains an aldehyde group which, from thermodynamical point of view, is more prone to the oxidation leading to the 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), as side product. Further oxidation of DFF and HMFCA led to high oxygen containing products such as 5-formyl-2-furancarboxylic acid (FFCA) and furandicarboxylic acid (FDCA), and thus the selectivity to DFF remains an issue to be overcome under mild conditions. Recent reports revealed the use of stoichiometric oxidants generating toxic wastes, [6] while the reported heterogeneous catalytic systems are active only in harsh reaction conditions [7].

Reports in selective oxidation of HMF to DFF under homogeneous catalysis indicated the behavior of different formulations, including Co/Mn/Zr/Br [8], vanadium [4,9], Mn(III)-salen [10] or Cu based catalysts [4,11–13]. Considerable efforts have also been made to find efficient heterogeneous catalysts for this synthesis, but without a real progress. Among these, Ru based catalysts showed better HMF conversions and DFF selectivities [14–17] in the presence of molecular oxygen, but at high pressure. However, the elevated price of noble metals entails the innovation of cheap transition metal-based heterogeneous catalysts. The use of vanadium supported on different oxides (TiO_2, MgO, Al_2O_3, zeolites) revealed an increased selectivity to DFF for a high VO_x surface density that was associated to the formation of small V_2O_5 crystallites [18,19]. The oxidation occurs also in the presence of air where, using toluene as solvent, a selectivity of 69% in DFF was reported working with very high weight catalysts/HFM ratios (2:1 wt/wt) [20]. Mn based catalysts

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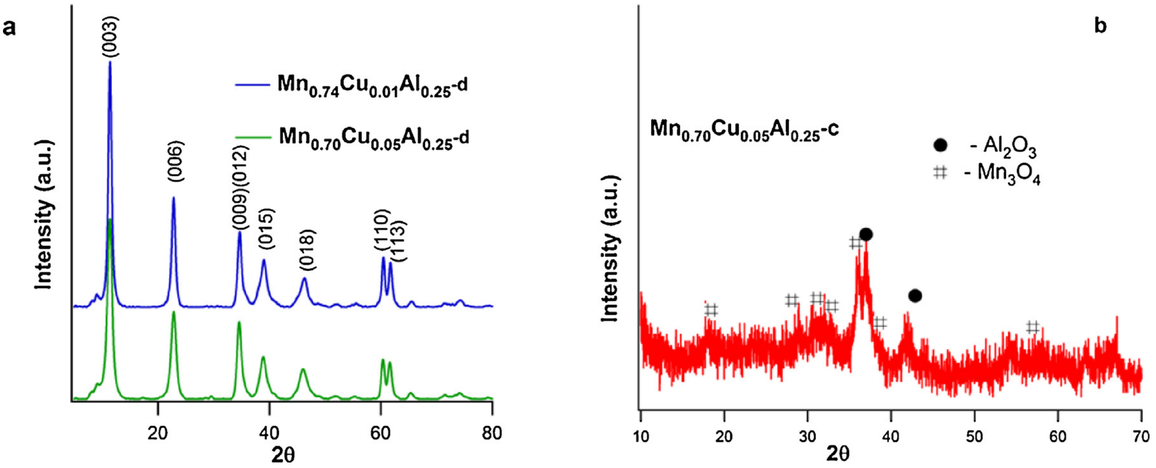
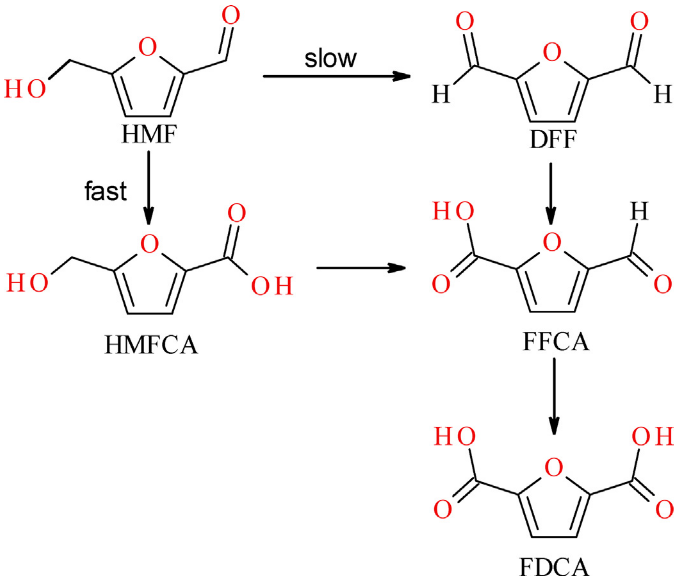


Fig. 1. X-ray diffraction patterns for: (a) dried $Mn_{0.74}Cu_{0.01}Al_{0.25}$-d and $Mn_{0.70}Cu_{0.05}Al_{0.25}$-d and (b) $Mn_{0.70}Cu_{0.05}Al_{0.25}$-c.



Scheme 1. Reaction pathways in oxidation of HMF (DFF: 2-diformyl furan; FFCA: 5-formyl-2-furancarboxylic acid; HMFCA: 5-hydroxymethyl-2-furancarboxylic acid; FDCA: furandicarboxylic acid).

were also investigated as an extension of the results in homogeneous catalysis [8,10]. The ability of manganese oxide for the oxidation of the hydroxyl group to a carbonyl one was well proved and good catalytic results in terms of conversion and selectivity were already reported over a wide series of manganese based catalysts [21]. Thus, cryptomelane-type manganese oxide (octahedral molecular sieve (OMS-2)) efficiently catalyzed aerobic oxidation of 5-HMF to 2,5-DFF with an yield as high as 97% at 110 °C in *N*,*N*-dimethylformamide as solvent [22]. The same oxidation was achieved [23] on K-OMS-2 with an almost total yield and selectivity using dimethyl sulfoxide as solvent.

Despite these achievements there are still aspects requiring optimization like the reaction temperature or replacement of the various solvents (DMF, DMSO, toluene, AcCN) with more innocent ones. The economical aspect including the nature of the selected active components is also very important.

Herein, we report a manganese-copper layered double hydroxide (LDH) catalyst for the oxidation of HMF to DFF under mild aqueous conditions. Besides the above mentioned role of manganese, copper was indicated for its activity at lower temperatures [4,11]. Taking the advantage of these achievements this study associated Cu and Mn, and a hydrophilic support like LDH, with the aim to overcome the temperature and solvent issues. Moreover, to date, in our best knowledge, no LDH-type catalyst has been reported for HMF oxidation.

2. Experimental

2.1. *Catalysts synthesis*

Layered double hydroxides containing two different compositions, namely $Mn_{0.74}Cu_{0.01}Al_{0.25}$ and $Mn_{0.70}Cu_{0.05}Al_{0.25}$, were prepared by a co-precipitation method. With this purpose two aqueous solutions were drop-wise simultaneously added into a flask under vigorous stirring at room temperature, while maintaining pH of 10. One of the solutions contained copper nitrate (0.015 M or 0.06 M, respectively), manganese nitrate (1.1 M or 0.8 M, respectively) and aluminum nitrate (0.3 M) in deionized water (180 mL), while the second contained sodium hydroxide (2.5 M) and sodium carbonate (1 M) in deionized water (180 mL). The slurry was aged for 18 h at 75 °C, and the final precipitate was filtered, thoroughly washed until pH 7 and dried overnight at 100 °C in oven. All the catalysts were investigated (i) as prepared- denoted with “d”, (ii) calcined at 460 °C under static air –denoted with “c”, and (iii) in the rehydrated form- denoted with “r”. The rehydrated samples were firstly calcined at 460 °C under static air, and then hydrated with bidistillated water at room temperature for 24 h. The slurry was then dried overnight at 100 °C in air atmosphere. The same co-precipitation procedure was used for the synthesis of catalysts containing only manganese and aluminum, $Mn_{0.75}Al_{0.25}$. This catalyst was used in the dried and calcined forms. Separately, pure manganese, aluminum and copper oxides were prepared by the same procedure.

2.2. *Catalysts characterization*

The characterization of the porous texture of the calcined samples was performed by N_2 adsorption at −196 °C. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area from the data obtained at P/P_0 between 0.01 and 0.995. Prior to surface area determination, all powders were degassed at 150 °C for 5 h. The pore size distribution of each sample was determined from the desorption branch of the N_2 isotherm, using a Micrometrics instrument (ASAP 2010).

The crystalline phases of the powder catalysts were examined by X-ray powder diffraction (XRD) performed using a Shimadzu XRD-7000 diffractometer with Ni-filtered monochromatic Cu Kα1

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