Selective synthesis of 2, 5-furandicarboxylic acid by oxidation of 5-hydroxymethylfurfural over MnFe$_2$O$_4$ catalyst

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ABSTRACT

Development of green catalytic processes using biobased feedstock for valuable chemicals such as 5-hydroxymethylfurfural (HMF) is hotly pursued. 2, 5-Furandicarboxylic acid (FDCA), a bio-based alternative to terephthalic acid was efficiently synthesized by oxidation of HMF using MnFe$_2$O$_4$ spinel structured magnetic nanoparticles (MNPs) and *tert*-butyl hydroperoxide as an oxidant. MnFe$_2$O$_4$ catalyst showed the highest activity and selectivity and gave 85% yield of FDCA at 100 °C in 5 h. The higher activity of MnFe$_2$O$_4$ catalyst is due to the variable oxidation state of manganese. The combination of MnFe$_2$O$_4$ catalyst and TBHP oxidant requires less time and energy compared to other reported processes of FDCA synthesis. Also, many reported methods have used a homogeneous base for FDCA synthesis which is totally avoided in the current process. The concentration profiles of reactants and products were established and kinetics determined. The effects of various reaction parameters were studied to validate kinetic model. The catalyst was easily recycled due to its magnetic property and showed good catalytic activity up to four cycles. All metal ferrites were characterized by different analytical techniques. The catalyst maintained its fidelity.

1. Introduction

Nowadays, the use of biomass is gaining importance for the synthesis of value added chemicals due to the depletion of fossil raw materials [1–3]. In this regard, 5-hydroxymethylfurfural (HMF) and its derivatives play a vital role. HMF is derived from sugars like fructose and glucose after triple dehydration by using acid catalysts [4,5]. It can be further valorized into various useful chemicals such as levulinic acid, 2, 5- dimethylfuran (DMF), γ-valerolactone, 2, 5-diformylfuran (DFF) and 2, 5-furandicarboxyllic acid (FDCA) [6–9]. From these chemicals, the oxidation product of HMF i.e. FDCA is one of the promising chemicals because of its potential use in polymer industry. It acts as an alternative for terephthalic acid, which is used in the synthesis of polyethylene terephthalate (PET) [10,11]. PET is widely used in synthesis of plastic bottles, food containers, fibers, photographic films, agrochemicals, pharmaceuticals and cosmetics [12,13]. Similar to terephthalic acid, FDCA can also transformed into poly (ethylene 2, 5-furandicarboxylate) (PEF) polymer, which has similar properties to PET [14]. In accordance with U.S. department of energy, FDCA can act as one of the twelve key platform chemicals obtained from biomass [15].

Till now, many processes are reported for production of FDCA by using homogenous and heterogeneous catalysts. Homogenous catalytic processes involved the use of KMnO$_4$, K$_2$Cr$_2$O$_7$, Co(OAc)$_2$/Zn(OAc)$_2$/

Br$^-$ [11] and metal/bromide salts [16]. All these methods produce toxic metal waste after their use and thus are not convenient for FDCA production. Several heterogeneous catalytic processes are also reported for FDCA synthesis. Usually these methods involve the use of noble metals like Pt, Au or Ru and addition of liquid base. Supported platinum catalysts consist of Pt/Al$_2$O$_3$ [17], Pt/ZrO$_2$ [11], Pt/C with Bi as a promoter [6] and Pt nanoparticles with PVP as a stabilizer [18]. Gold catalysts used for HMF oxidation consist of Au/TiO$_2$ [19], Au$_3$Cu$_1$/TiO$_2$ [20] and Au-Pd alloy supported on carbon nanotube [21]. These catalysts give good yield of FDCA but are expensive and require addition of liquid base NaOH and high oxygen pressure. Recently, Gupta et al. demonstrated base-free oxidation of HMF into the FDCA by using Au/HT catalyst [13]. However, magnesium is found to leach out from the support hydrotalcite (HT) due to interaction of acidic product FDCA and basic hydrotalcite. Davis et al. used carbon nanofibres (CNF) supported Pt and Au catalyst for HMF oxidation [22]. Gorbanev et al. used ruthenium based catalysts in which Ru(OH)$_X$ was supported on various supports like TiO$_2$, ZrO$_2$, CeO$_2$, MgO$_2$, La$_2$O$_3$, Al$_2$O$_3$, HT and hydroxyapetite by using dioxygen as oxidant [23]. The catalytic processes other than noble metal such as, Fe^{III}-POP-1 [24] and CuCl [25] are also reported for FDCA production. Recently Neatu et al. reported FDCA synthesis by using Mn/Fe mixed oxide in presence of NaOH base [26]. FDCA can also be directly obtained in one pot from fructose by using

cobalt acetylacetonate [27] and various other catalysts [28]. Many of above reported method includes addition of liquid base, high temperature and high pressure for oxidation of HMF into FDCA. The problem associated with usages of base at high temperature is the degradation of HMF to undesirable products and hence making the process uneconomical. So there is a need to develop a heterogeneous catalytic process for HMF oxidation at ambient reaction conditions. Also, the use of stoichiometric oxidants like hydrogen peroxide (H_2O_2) and *tert*-butyl hydroperoxide (t-BuOOH) with heterogeneous catalyst is limited for this reaction. Only a single homogeneous method is reported in which Hansen et al. used t-BuOOH and CuCl in presence of nitrogen containing promoters [25]. This method produces large amount of wastes and so it is not clean and economical.

Here we have developed a mild and energy efficient process for FDCA synthesis. Various metal ferrite MFe_2O_4 (M = Cu, Mn, Co, Mg) were synthesized by hydrothermal method and used for HMF oxidation along with t-BuOOH as a stoichiometric oxidant. Because of the nano size and magnetism of spinel ferrites, their use as catalysts is gaining impetus in various organic reaction transformations [29–31]. Spinel ferrites also exhibit other advantages such as stability at higher temperature, easy separation from reaction mixture, monodispersity, and low cost [32]. TBHP is a highly active oxygen containing cheaper and environmental friendly oxidant because its reduction product is *tert*-butyl alcohol which can be easily removed from reaction mixture [33]. Among all metal ferrites, $MnFe_2O_4$ was found to be most active and selective for FDCA synthesis. This catalytic system is better than other reported processes as no external base was added during the reaction. The catalyst was simply separated by using external magnet from reaction mixture and so it prevents catalyst loss which occurs in filtration and makes the process more economic. The concentrations of all intermediates observed in this reaction were determined and kinetic data obtained. Various reaction parameters were studied and a kinetic model successfully developed.

2. Experimental section

2.1. Chemicals

All chemicals were purchased from commercial sources except HMF which was procured from Acros Organics (India) and no further purification was done before the use of all chemicals.

2.2. Catalyst synthesis

All metal nano particles (MNPs) were synthesized by hydrothermal method as reported earlier [31,34,35]. A brief process is given in which 10 mmol $FeCl_3 \cdot 6H_2O$ and 5 mmol $MCl_2 \cdot 4H_2O$ (M = Cu, Co, Mn, Mg, Fe) were dissolved in 150 mL ethylene glycol. Then, in this clear solution were added 7 g NaOAc and 2 g polyethylene glycol and the resulting solution was stirred for 1 h. Then it was transferred into teflon lined stainless steel bomb and heated at 200° C for 10 h to produce a black material. After cooling at room temperature, the black material was washed with ethanol and dried at 100° C for 5 h. Ethylene glycol was used as a solvent for catalyst preparation due to its surfactant property which prevents the agglomeration of MFe_2O_4 MNPs.

2.3. Experimental setup

All reactions were carried out in 100 cm^3 autoclave (Amar autoclave, Mumbai) equipped with a pitched turbine impeller. A standard reaction was carried out with 1 mmol of HMF, 9 mmol of TBHP and 0.015 g/cm^3 of catalyst loading which was made up to 20 mL by adding acetonitrile as solvent. The reaction mixture was heated at 100° C and agitation speed maintained at 1000 rpm. Sampling was done at regular intervals for further analysis.

2.4. Method of analysis

The reaction samples were analyzed by using HPLC (Agilent 1260 infinity) equipped with Agilent Hi-plex H column (300 × 7.7 mm).A 0.005 M H_2SO_4 solution was used as mobile phase with 0.5 mL/min flow rate. All compounds were identified by calibrating authentic commercial samples on UV and RI detectors.

3. Results and discussion

3.1. Catalyst characterization

The characterization of MFe_2O_4 was performed by various analytical techniques like XRD, BET surface area, GA, FTIR, SEM and TEM.

3.1.1. X-ray powder diffraction (XRD)

The textural properties and crystallinity of MFe_2O_4 spinel ferrites were studied by using XRD. The powder XRD patterns of all catalysts were performed on X-ray diffractometer (Bruker AXS, D8 Discover, USA) with Cu Kα radiation. The crystal structure of the mesoporous spinel ferrite nanospheres were analyzed via X-ray powder diffraction measurements. Fig. 1 shows typical XRD patterns of various MFe_2O_4 (Co, Mg, Mn, Cu & Fe) nanospheres. The XRD analysis reveals that all samples show the spinel cubic structure, exhibiting six prominent peaks 2θ = 30.1, 35.4, 43.1, 50.3, 53.2, 62.6, and 74.08 which originate from the (220), (311), (400), (422), (511) and (440) planes, which reflects cubic spinel structure of all MFe_2O_4. The diffraction patterns perfectly match with the expected cubic spinel structure of Co, Mg, Mn, Cu and Fe ferrites and have been identified as (JCPDS 22-1086), (JCPDS 89-3084) (JCPDS 38-0430), (JCPDS 34-0425), and (JCPDS 19-0629), respectively.

3.1.2. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra for all catalysts were obtained on a Perkin Elmer Spectrophotometer in the range of 400–4000 cm^{-1} (Fig. 2). The IR spectra for all MFe_2O_4 catalyst show two peaks in the range of 400 to 650 cm^{-1}, The absorption band at 446 cm^{-1} is that of tetrahedral M^{3+} (M-O mode) and at 634 cm^{-1} represents stretching vibration frequency of octahedral M^{2+} (M-O mode) complexes. The peak near 1100 cm^{-1} designates the C−O−C stretching vibration of ethylene glycol. The band near 1600 and 3500 cm^{-1} indicate the bending and stretching vibrations of water respectively.
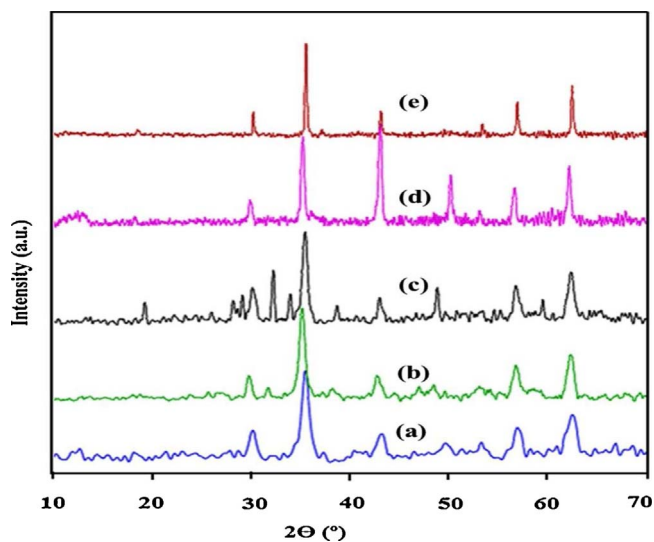

Fig. 1. XRD of different metal ferrite spinel catalysts (a) $CoFe_2O_4$ (b) $MgFe_2O_4$ (c) $MnFe_2O_4$ (d) $CuFe_2O_4$ (e) Fe_3O_4.