



Titania nanoparticles embedded in functionalized carbon for the aqueous phase oxidation of 5-hydroxymethylfurfural

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ABSTRACT

Titania nanoparticles have huge potential due to their low cost, easy preparation, separation and high catalytic application. As-synthesized titania nanoparticles embedded at the functionalized acidic carbon act as effective heterogeneous catalyst for the selective oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfuran (DFF) and 2,5-furandicarboxylic acid (FDCA) in water. It was found that the doping of Ti (IV) with sulfonated carbon improve the catalytic effectiveness of resulting materials. The oxidation reaction and selectivity of the oxidation products, DFF, FDCA and FFCA were monitored by use of oxygen through manometric apparatus and a GC chromatogram. Titania nanoparticles embedded at the functionalized carbon gave higher selectivity for DFF (88% yield) under 1 atmospheric pressure of O₂ at 70 °C. The catalyst was characterized by the XPS, XRD, FESEM, HRTEM, FTIR and Raman spectroscopic techniques. The characterization data reveal the presence of the acid sites and titania in +4 oxidation state.

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1. Introduction

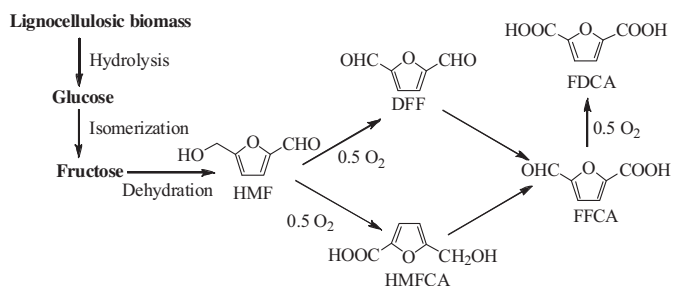
Conventional fossil based resources like coal, natural gas and petroleum are the sole and necessary resources for chemicals and energy production [1]. In today's world of fossil fuel crisis, reducing dependency on fossil fuels is a major challenge for economically developing countries of the world. Switching to alternative renewable energy sources, could leave a very serious impact on the world economy and the world's communities. Synthesis of chemical from renewable sources will provide a solution to the quick running down of mother earth fossil resources, the consciousness of environment change and the soaring volatility in crude oil price, caused by disproportion in demand-supply, has put remarkable pressure on the world economy [2–4]. Thus, novel synthetic routes and related technologies for producing chemicals from non-conventional resources are the thrust and cutting-edge research of the present generation. Catalytic transformations of biomass derived carbohydrates into chemicals via platform chemicals, 5-hydroxymethylfurfural (HMF), has received considerable courtesy [5–7]. Heterogeneous aqueous phase catalytic oxidation of HMF

is a very promising field of research due to the fact that such processes can easily be incorporated into pre-existing HMF technologies. The prospective of HMF can serve as platforms for a variety of renewable biomass-based chemicals, fuels and polymer industries. HMF is potentially available from a variety of biorenewable resources, including C₆ monosaccharide's, such as fructose, glucose, polysaccharides, as cellulose. HMF and its derivatives, such as 2,5-furandicarboxylic acid (FDCA), 2,5-Diformylfuran (DFF) and 5-Formyl-2-furancarboxylic acid (FFCA) have been identified as possible building blocks various products such as resins, composites, foams, adhesives, sealants, binders, solvents, monomers, and pharmaceuticals.

Terephthalic acid (TA) is the by product of *para*-xylene oxidation a petroleum based monomer, one of the most used dicarboxylic acid for the synthesis of polyethylene terephthalate polymer and products [8,9]. For that reason, chemical industries have shifted their centre of attention to the sustainable alternative of TA [10,11]. In recent years, FDCA has received considerable attention as an alternative substitute for petroleum based terephthalic acid for next generation polyester production [10,12]. FDCA based polymer called poly(ethylene 2,5-furandicarboxylate) (PEF) and it showed comparable thermal stability to PET [13,14]. The FDCA can be synthesized by catalytic transformation of cellulosic biomass to HMF [15], followed by liquid phase oxidation of HMF (Scheme 1) [16–18]. Scheme 1 shows, two possible routes for the HMF oxidation to FDCA

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Scheme 1. Possible HMF oxidation reaction sequence [19].

[19]. If oxidation of aldehyde occurs then HMFCFA is the intermediate product or if alcohol oxidized to give DFF as intermediate product. The liquid phase oxidation HMF and intermediate product also depends on catalyst and solvent. The liquid phase oxidation of HMF was examined with the metal acetate catalyst including cobalt acetate as catalyst, manganese acetate as co-catalyst and a bromide as promoter, at high temperature and pressure using nature unwanted acetic acid as solvent [20], mentioned that hydroxymethyl group of HMF being oxidized more preferentially than the aldehydes group [19]. Similar observation was also reported by Saha et al., by using cobalt acetate, zinc acetate and sodium bromide as catalyst for the oxidation of HMF [17]. The oxidation of HMF has also been reported with the different heterogeneous catalysts. Vinke et al. used alumina supported platinum catalyst ($\text{Pt}/\text{Al}_2\text{O}_3$) as catalyst for the HMF oxidation and they reported 5-formyl-2-furancarboxylic acid (FFCA) as the sole product [21]. In a successive communication, the authors also demonstrated near quantitative FDCA yield and selectivity with the same catalyst ($\text{Pt}/\text{Al}_2\text{O}_3$), in the extra addition of base [22]. Oxidation of HMF using Pt/ZrO_2 as catalyst was investigated by Lilga et al. and they claimed, 68% DFF and 32% FFCA selectivity, respectively [23]. One-pot synthesis of FDCA was also reported by using PtBi/C , $\text{VO}(\text{acac})_2$ and $\text{Co}(\text{acac})/\text{SiO}_2$ as catalysts [24,25]. However, these processes have limitation to use precious metal (Pt, Pd or Au) or homogeneous non-recoverable metal salt, at harsh reaction conditions.

Heterogeneous metal (Au/TiO_2) catalyst has been also explored for HMF oxidation 98% esterified FDCA in methanol at 130°C and 4 bar pressure [26]. Conversely, in this reaction extra addition of base is also required. The role of a base additive (NaOH), was also essential in with noble metal (Au/TiO_2 and Au/CeO_2) supported catalytic oxidation of HMF, exclusive of that poor selectivity FDCA reported [27,28]. In comparison to base, Saha et al., were reported an acid additive (HTFA) based technique for HMF oxidation in presence of Au/TiO_2 and Au/CeO_2 as catalyst in acetic acid solvent, although use of acetic acid as solvent was not a great choice [17]. Although various homogeneous metal salts and heterogeneous metal catalysts have been reported for the HMF oxidation, the carbon supported Brønsted acidic titania (IV) catalyst for efficient oxidation of 5-hydroxymethylfurfural in waters is not known. In this paper, we disclose the synthesis and catalytic application of renewable carbon supported carbonaceous material, containing Brønsted acidic sulfonic acid group and Ti(IV) mesopores, (henceforth referred as CSTi) for aerobic oxidation of HMF using pure oxygen as oxidant in water.

2. Experimental

2.1. Materials and methods

All the chemicals were of high purity. Glucose, HMF, *p*-toluenesulfonic acid and Titania isopropoxide were purchased from Sigma–Aldrich and used as received. Methanol was purchased

from Merck, India. Authentic samples of DFF, FDCA and FFCA were obtained from TCI, India and analyzed as received. Unless otherwise mentioned, all experiments were carried out in double distilled water.

2.2. Preparation of carbon supported Brønsted acidic titania (IV) catalyst

Carbon supported Brønsted acidic titania (IV) catalyst is synthesized in one-pot method, for this, glucose, *p*-toluenesulfonic acid and titania (IV) isopropoxide were mixed in 1:1:04 ratio, and transferred in Teflon-sealed autoclave, and maintained the temperature of the mixture at 180°C for 24 h as reported elsewhere [15]. As-synthesized material was ground to powder and washed with hot water-ethanol (1:1) solution and dried in oven at 100°C for overnight and denoted as CSTi. Another reference material was also prepared under similar conditions without adding Titania (IV) isopropoxide, denoted as CS.

2.3. Instruments

The material properties of as-synthesized CSTi was analyzed by X-ray Photoelectron Spectra (XPS, PHI5000 Versa Prob II, FEI Inc.) equipped with Auger Electron Spectroscopy (AES) module and C60 sputter gun. The sample charging during the measurement was compensated by an electron flood gun. The electron take off angle with respect to the sample surface was 45° . The XPS spectra were collected in a fixed analyser transmission mode at 89.45 and 35.75 eV for recording survey and high resolution spectra, respectively. The Fourier Transform Infra Red (FTIR) spectrum of CSTi material was recorded on a Perkin-Elmer FTIR 2000 spectrometer using KBr disc, at $4000\text{--}400\text{ cm}^{-1}$ range. Nitrogen adsorption/desorption isotherms obtained by using a Beckman Coulter SA 3100 Surface Area Analyzer at 77 K. Prior to adsorption measurement the samples were degassed in vacuum at 180°C for about 3 h. Absorption spectra were recorded using a Perkin-Elmer Lambda-25 spectrophotometer. Thermal gravimetric analysis (TGA) and differential thermalgravimetric analysis (DTA) of the Solid acid catalyst was performed on DTG-60 SHIMADZU at a heating rate of $10^\circ\text{C}/\text{min}$ heating rate from 30°C to 700°C under a nitrogen atmosphere. Raman analysis was carried out using a Renishaw Raman RM 1000 spectrometer (Renishawplc, Gloucestershire, UK), equipped with a Leica research microscope. A $20\times$ magnifying lens was used for analysis. All measurements were performed at excited wavelength of 514.5 nm using an argon ion laser source (maximal output 20 mW). The samples were run in the frequency range of $4000\text{--}400\text{ cm}^{-1}$. Powder X-ray diffraction (PXRD) patterns were recorded using a BrukerAXSD8Discover (Cu-K α radiation, $\lambda = 1.54184\text{ \AA}$) diffractometer at room temperature. The samples were ground and subjected to the range of $10\text{--}70^\circ$ with a step size of $1^\circ/\text{per minute}$ in 2θ angle. Transmission electron microscopy (TEM) analyses were performed with a Philips Technai G230 operating at an accelerating voltage of 200 kV. Samples suitable for TEM observation were prepared by applying one drop of dilute as-prepared CSTi catalyst dispersion in ethanol onto the carbon coated Cu grid and allowing the solvent to slowly evaporate at room temperature. Scanning Electron Microscope (SEM)-Zeiss was used for the determination of morphology of CSTi materials. CHNS, elemental analyses were performed on a Elementar Analysensysteme GmbH Vario EL-III instrument.

2.4. HMF oxidation

Liquid phase oxidation of HMF was performed under atmospheric oxygen in a manometric glass reactor equipped with magnetic bar for oxygen saturation in the solution. Initial rates of

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