Application of Polyoxometalate in Synthesis of 2,5-Diformylfuran and Its Derivatives

Zheng Li

Beijing Institute of Technology, Beijing, 102488, China

2120171262@bit.edu.cn

Abstract: Because of the inherent defects of fossil resources, replacing fossil resources with biomass resources is a great challenge in the 21st century. 2,5-Diformyl furan (DFF) and its derivatives are important value-added chemicals derived from biomass platform chemicals 5-hydroxymethylfurfural (HMF) and fructose, which have great application in the field of medicine, biopolymer and scientific research. It is of great significance to select suitable catalyst to complete the conversion. Polyoxometalate is anionic metal oxide clusters, due to their excellent thermal stability and redox ability, polyoxometalate are widely used in catalytic oxidation and have been gradually used in biomass value-added conversion. The preparation of DFF and its derivatives from HMF and fructose using polyoxometalate has become a research hotspot in recent years.

1. Introduction

With the expansion of the global economy, the demand for energy, chemicals and materials is increasing, resulting in the over exploitation of fossil resources and environmental pollution[1]. Therefore, a major challenge to the 21st century is to replace fossil products with sustainable alternatives. Biomass resources are one of the most abundant renewable resources, which have attracted much attention because of their universality and diversity in nature. According to the statistics, the annual output of biomass resources in nature is about 170 billion tons. Among them, derived from C6 carbohydrate dehydration, 5-hydroxymethylfurfural (HMF) is one of the most promising and important platform chemicals originated from biomass[2], several value-added chemicals including 2,5-furandicarboxylic acid (FDCA), 2,5-diformyl furan (DFF), Maleic acid (MA), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) and 5-formyl-2-furancarboxylic acid (FFCA) can be can be obtained respectively by selective oxidation of HMF or fructose. Such DFF and its derivatives are widely used in medicine, material and scientific research[3-5]. Polyoxometalate are composed by cations and diversity structural polyanion clusters, its unique structure endows it with excellent acid-base property, redox property, excellent thermal stability and oxidation stability, which makes it has an important application in the field of oxidation catalyst and has been widely used in the value-added transformation of biomass resources[6]. Recent works on the synthesis of DFF and its derivatives from HMF and fructose using polyoxometalate were discussed briefly.

2. Synthesis of 2,5-diformylfuran and its derivatives using polyoxometalate

2.1. synthesis DFF and its derivatives from HMF
As an important chemical, maleic acid has important applications in the production of tartaric acid, fumaric acid, succinic acid, DL malic acid, dyeing auxiliaries, medicine, pesticide food manufacture of unsaturated polyester resin and it is also widely used in medicine, pesticide and food. Yin and co-workers studied the preparation of maleic anhydride and maleic acid from HMF oxidation using Keggin type Heteropolyacids-HPA-2 (H₄PV₂Mo₁₀O₄₀) [7]. Under the optimized conditions (acetonitrile/acetic acid, 10 atm O₂, 363 K, 8 h), 64% total maleic anhydride and maleic acid yield was obtained. The contrast experiment shows that the formation of maleic acid and maleic anhydride was began with the C-C bond cleavage between aromatic ring of HMF and hydroxymethyl group catalyzed by HPA-2, rather than the oxidation of aldehyde and hydroxyl groups of HMF, a new mechanism for the formation of maleic acid and maleic anhydride was proposed by this work.

FDCA is the most important chemicals in the HMF oxidation products and the most important application of FDCA is as the key building block of bio-polymer. Li and co-workers studied the oxidation of HMF to FDCA using quaternary ammonium octamolybdate (Mo₈O₂₆) and quaternary ammonium dectungstate (W₁₀O₃₂) with hydrogen peroxide in the absence of organic solvent[8]. Quaternary ammonium octamolybdate ([EMIM]₄Mo₈O₂₆, [CTAB]₄Mo₈O₂₆, and [EPy]₄Mo₈O₂₆) demonstrates excellent activity for HMF oxidation, 100% FDCA selectivity at 99.5% HMF conversion was achieved using [EMIM]₄Mo₈O₂₆, while the massive use of sodium hydroxide limits its industrial application. The authors found that quaternary ammonium ([EMIM]Br, EPyBr and CTAB) weakened the oxidative cleavage of HMF and promoted the contact between the catalyst and HMF while due to structural difference of polyanion clusters, quaternary ammonium dectungstate ([EMIM]₄W₁₀O₃₂, [CTAB]₄W₁₀O₃₂, and [EPy]₄W₁₀O₃₂) were unfavorable for FDCA formation. Recently, Great progress has been made by Zhang and co-workers in efficient base-free oxidation of HMF to FDCA[9]. The authors reported a novel catalytic system using ionic liquids and heteropoly acids (ILs-HPAs), HPAs shows high activity for the oxidation of HMF, imidazole ionic liquids promoted the contact between HMF and the active center of catalysts and also prevented oxidative cleavage of HMF, finally 89% yield of FDCA was reached using HPMV₆ and [Bmim]Cl under optimized reaction conditions, meanwhile, ILs-HPAs exhibited moderate activity in the direct synthesis FDCA from carbohydrates and 48% yield FDCA was obtained from glucose.

Because FFCA is the intermediate product of the production of FDCA from HMF oxidation, it is difficult to obtain FFCA selectively though the oxidation of HMF, thus there are few reports on the preparation of FFCA by selective oxidation of HMF. Lv and co-workers adopted a method using a Fe-Anderson type polyoxometalate of Na₃H₆FeMo₆O₂₄·5H₂O to selective oxidize HMF to FFCA[10]. The experimental results reveal that N-methyl pyrrolidone (NMP) is the most suitable solvent for selective oxidation of HMF to FFCA. Under the optimal conditions (HMF/K₂CO₃/Catalyst = 1/0.5/0.08, T = 373 K, 8 h), 75% yield of FFCA could obtained under atmospheric oxygen.

Heterogeneous catalysis of polyoxometalate is also a hot topic for researchers. Chen and co-workers prepared and characterized a series of acidic cesium salts of molybdovanadophosphoric heteropolyacid (CsMVP-HPAs) as bifunctional and recyclable catalysts[11]. Among CsMVP-HPAs, Cs₈HPMo₁₀₁VO₄₀ exhibited excellent activity for selective oxidation HMF to DFF in DMSO with the mass ratio of HMF to catalyst was 120:150 under optimized conditions (413K, 0.8MPa O₂), finally 99% yield of DFF was obtained after 6 hours of reaction, furthermore, as a bifunctional catalyst, CsMVP-HPAs shows high activity for a one-step synthesis DFF from fructose with molecular oxygen as the oxidant which will be discussed in the next section. Wang and co-workers prepared H₃PMo₁₀₁V₂O₄₀/SiO₂ (HPMoV/SiO₂) nanofibers with a mesoporous structure using electrospinning and surfactant-directing pore formation technique[12], 89.2% yield of DFF was obtained using HPMoV/SiO₂ as heterogeneous catalyst under optimized conditions(393 K, 1 MPa O₂) after 8 h of reaction. Furthermore Wang and co-workers prepared and characterized HPMoV@surf(n)/CeO₂ nanofiber hybrids material[13]. Polyoxometalate (H₃PMo₁₀₁V₂O₄₀) modified CeO₂ electrospun nanofiber shows better performance in the charge transfer and tolerance to changes of the surrounding environment due to the interaction between Ce and metal sites (V) in H₃PMo₁₀₁V₂O₄₀, meantime the rich redox sites, basic sites and Lewis sites in the HPMoV@surf(n)/CeO₂ nanofiber hybrids make it shows excellent activity in the aerobic oxidation of
HMF to DFF, finally 95.3% DFF yield at 100% HMF conversion was obtained using HPMoV@surf(4)/CeO2(30 wt%) and catalyst could be recycled at least 10 times. Wang and co-workers also synthesized H5PMo10V2O40/chitosan nanofibers using the electrospinning method and the prepared catalyst was characterized systematically[14]. Polyoxometalate modified chitosan nanofibers combined the redox ability of polyoxometalate and the high specific surface area and basicity of nanofiber structure, which makes it exhibits excellent performance in catalytic selective oxidation of HMF to DFF. The experimental results show that the activity of H5PMo10V2O40 modified chitosan nanofibers for selective oxidation of HMF to DFF reaches the maximum when H5PMo10V2O40 loading amount was 3.5 mmolg\(^{-1}\). 94.1% yield of DFF in DMSO and 56.2% yield of DFF in aqueous solution were obtained under the optimized conditions, and the prepared H5PMo10V2O40/chitosan nanofibers catalysts can be recycled and reused for at least 10 times without significant loss of activity, but a small amount of polyoxometalate (<1.5%) could be leached from H5PMo10V2O40/chitosan nanofibers catalysts.

Due to the mild reaction conditions, low energy consumption and air as green oxidant, photooxidation of HMF has gradually aroused the interest of researchers. Zhang and co-workers first adopt decatungstate as an efficient polyoxometalate photocatalyst under visible light oxidize HMF with O2 in MeCN under mild condition of temperature and pressure[15], the authors found that NaBr, DMSO and [Bimi]Cl can restraining effect on the light-induced HMF polymerization, water and some strong acid solutions play a positive adjusting effect on this photo-catalytic oxidation and 67.1% DFF and 5.8% FDCA yields as well as 87.7% carbon balance yield was achieved with HBr as additive.

2.2. synthesis DFF from fructose

The preparation of DFF from fructose is a tandem reaction, which usually requires bifunctional catalyst. In order to complete the formation of HMF from fructose and subsequent oxidation of HMF to DFF, high Bronsted acidity and appropriate redox potential are needed for bifunctional catalysts. Polyoxometalate usually contain many active sites such as protons, oxygen and metals, which is the ideal bifunctional catalyst.

As mentioned above, the bifunctional and recyclable catalyst CsMVP-HPAs prepared by Chen and co-workers achieved the direct synthesis of DFF from fructose[11]. Under the synergistic effect of acidic site (H) and metallic site (V), 60% yield DFF was obtained from fructose using Cs3HPMo11VO40 as bifunctional heterogeneous catalyst under atmospheric oxygen, the authors found that the acid density and V content of CsMVP-HPA affect dehydration of fructose and subsequent oxidation of HMF respectively. When the ratio of acid concentration to V molar concentration is 1.64-3.34, the highest DFF yield could be achieved. Lee and co-workers using phosphomolybdic acid encapsulated in MIL-101 (PMA-MIL-101) as bifunctional catalyst synthesis DFF from fructose and a satisfactory DFF yield of 75.1% was obtained in a one-pot and one-step reaction under optimal reaction conditions[16]. Hu and co-workers prepared H3PMo12O40 (PMo12) heteropolyacid modified formyl-functionalized PAN (F-PAN) and polyaniline (PAN) bifunctional heterogeneous, under optimal reaction conditions (413 K for 7 h), 76.7% yield of DFF is obtained in atmospheric oxygen using the 40-PMo12/F3-PAN[17]. Zhou and co-workers prepared and characterized polyoxometalates modified mesoporous poly (ionic liquid) heterogeneous catalysts (PMoV2@CP-5.5-400)[18]. H5PMo10V2O40 heteropolyanion was introduced by ion-exchange with the carbon precursor CP-5.5-400. The redox and acidic properties of the catalyst are greatly enhanced due to the partial carbonization of polyoxometalate, thus PMoV2@CP-5.5-400 shows excellent activity in the preparation of DFF from fructose by one-pot and one-step method. Finally, 87.3% DFF yield and 77.7 turnover number was achieved using PMoV2@CP-5.5-400, the catalyst also showed good activity for other carbohydrate substrates such as sucrose and inulin.

3. Conclusion and Perspective

With great potential to replace fossil resources and great application prospect, DFF and its derivatives are important chemicals derived from biomass platform chemicals HMF and fructose. Therefore, the efficient conversion of biomass-derived HMF and fructose to value-added DFF and its derivatives is of great significance to the increasingly exhausted resources and energy, which is in line with the concept
of green chemistry and sustainable development. Recently, polyoxometalate have been gradually applied to the synthesis of DFF and its derivatives from biomass-derived HMF and fructose due to their excellent catalytic properties and satisfactory results have been achieved, DFF and its derivatives can be obtained with high selectivity under different conditions using polyoxometalate, noble metal free makes it more likely to the application in the industry. Although significant achievements have been obtained, harsh reaction conditions, high energy consumption and difficulty in separation of catalyst and product limit its practical application, thus heterogeneous catalytic oxidation and photocatalytic oxidation of polyoxometalate have high research value.

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