

Conversion of Cellulosic Biomass into high-value Chemicals & Fuels: A perspective of Heterogeneous and Electrochemical Catalysis

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Introduction

Since few decades fossils such as coal, oil and natural gas are being traditionally used to produce electricity, heat, and transportation fuels as well as vast majority of chemicals. Currently, industrial economies are being largely dependent on crude oil which provides the basis of most of our energy and chemical feedstocks – in fact, over 90% (by weight) of all organic chemicals are derived from petroleum [1] and 85% of crude oil consumed is used for the production of transportation fuels [2, 3]. However, crude oil reserves are finite and their demand in the world is growing [4]. In the meantime, there is an increasing concern over the impact of these traditional manufacturing processes on the environment (i.e. the effect of CO₂ emissions on global warming) [5]. At the same time irregular declining of these non-renewable carbon based fossil resources alarms many researchers towards alternatives. While much attention is paid to renewable energy such as wind [6], solar [6] and geothermal, but none of these renewable sources can be used to produce organic chemicals which are currently derived from fossil fuels. However, carbon-containing molecules found in re-newable biomass could potentially serve as a sustainable feedstock for the chemical industry. Biomass is one of the alternatives and the only accessible non-fossil source of carbon that can be processed into liquefied high value chemi-cals. These are easily incorporated into the existing transportation fuel infrastructure and to substitute the present fossil based chemicals and polymers [7]. The carbohydrates occur predominantly in nature in the form of biopolymers such as cellulose, hemi-cellulose, and lignocelluloses [8]. Therefore we aim to convert cellulosic biomass into 5-hydroxymethylfurfural (HMF) and then HMF is subjected to oxidation, reduction reactions by heterogeneous and electrochemical catalysis. HMF is expected to play a major role in new generation renewable based chemicals and its oxidative products 2,5-furandicarbaldehyde (FDC) and 2,5-furandicarboxylic acid (FDCA) are excellent candidates as monomers for the development of novel polymeric mate-rials. In fact FDCA has grabbed the attention as a potential replacement for terephthalic acid in the future. The reduction of HMF results 2,5-dimethylfuran (DMF), which has a number of attractions as a biofuel. DMF has an energy den-sity 40% greater than ethanol, making it comparable to gasoline (petrol). Levulinic acid (LA) produces upon hydration of HMF, which is useful as fuel additive. The total reaction scheme is shown in fig 1.

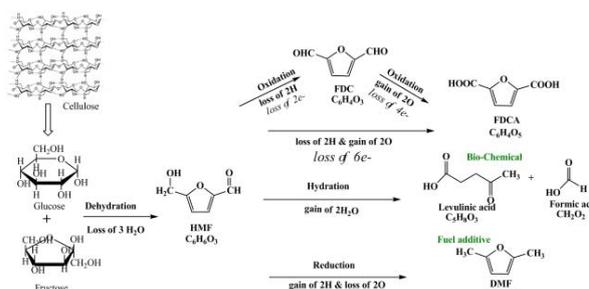


Fig 1. Conversion of cellulose into high-value chemicals & Fuels
The total reaction scheme is shown in fig 1.

Experimental

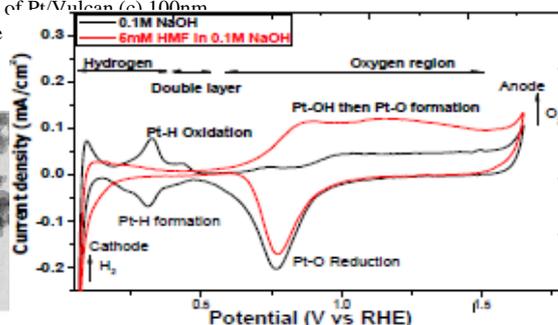
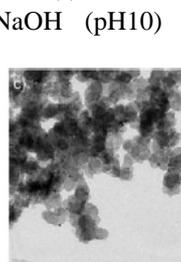
Heterogeneous catalysis was carried out in high pressure autoclave made-up with hastelloy and electrochemical reactions were conducted in electrochemical cell. Gamry reference 600 potentiostat has been used for variation of potential and current during electrochemical reaction. The working electrode of different pure metal foils (Pt, Pd, Ni) with 4.5 cm² geometrical surface area, reference electrode RHE and counter electrode Pt gaze (100mesh) has been used. The data was recorded using Gamry framework and analyzed by Gamry Echem Analyst software. The analysis of reaction mixture was conducted using Agilent's (6120 series) LC-MS equipped with UV/Vis, RID and MS detectors.

Results and Discussion

Cellulose conversion into HMF is a dehydration reaction and carried out using acid catalysts. The oxidation and reduction reactions of HMF are conducted using solid metals supported on carbon for heterogeneous reactions and metal electrodes for electrochemical reactions. The X-ray diffraction (XRD) and Transmission electron microscopy (TEM) were used for characterization of 20%Pt/Vulcan, Ni/Vulcan, Ru/Vulcan, Pd/SiO₂, Pt/Al₂O₃ and Rh/C catalysts prior to their application in oxidation and reduction reactions. Fig 4 shows cyclic voltammogram of Pt foil in different supporting electrolytes along with 5mM HMF at scan rate of 50mV/s. Pt surface is clear in supporting electrolyte with Pt-O reduction at 7.5 V/RHE in cathodic direction, H₂ desorption, evolution and adsorption peaks. Whereas in the presence of 5mM HMF, CV shows the adsorption of HMF on the surface of the electrolyte and oxidation peaks in anodic direction.

Then chronopotentiometry was carried out at 0.44mA/cm² current densities in electrochemical HMF electrolyte in 0.3M NaClO₄+0.1mM NaOH (pH10) supporting electrolyte. The electrolyte was purged for 10 min and blanketed with N₂ gas. The system was stirred with magnetic stirrer

Fig 2. TEM images of Pt/Vulcan (c) 100nm scale, (d) 10nm scale



and samples were collected for every 2 hrs and analyzed using LC-MS. In case of Pt the yield of desired oxidative product FDC increases to 18% and conversion of HMF to 70% with reaction time of 12hrs as shown in Fig 5. The selectivity of FDC

increases to 29% and then decreased.

The other oxidative products FFCA and FDCA are also formed but less than 1%. In the same way the electrocatalysis was conducted for Ni, Pd electrodes for their anodic oxidation of HMF. This paper extensively discusses the advantage and effect of electrocatalysis for oxidation and reduction reactions of biomass conversion with studying various effective parameters like effect of various potentials, current densities, type of metal electrodes, supporting electrolyte, effect of active surface area, pH, temperature, gases, etc.

At the same time, heterogeneous catalysis reactions are conducted in autoclave using molecular oxygen and hydrogen for oxidation and reduction reactions of HMF. 5mM HMF is oxidized using 25mg of 20%Pt/Vulcan catalyst under 10 bar O₂, 1600 rpm stirring speed and at 50°C. The reaction mixture was collected at regular intervals of time and was analysed using LC-MS.

HMF alone is not stable in pH13 solution, but in the presence of heterogeneous catalyst, HMF was oxidized directly into valuable FDCA. Within one hour of reaction time, 100% of HMF was converted into 50% FDCA and 18% FFCA without any significant formation of FDC as shown in fig 6. But more amount hemiacetal form of FDC was observed in LC-MS. As the reaction time progresses FFCA and hemiacetal are slowly converted into FDCA. Therefore reaction rate of FDCA formation is greatly affected by pH of the solution and nature of catalyst. This paper also discusses the effect of other metal catalysts *Pd, Ni, Ru, Rh, Mn* on different supports at different reaction conditions for selective oxidation and reduction of HMF into desired chemicals and fuels, and their kinetic information. Our main focus is to establish a relationship between electrode potential/current densities to the conversion/selectivity which will guide the selection of suitable reaction conditions for a heterogeneously catalyzed biomass conversion processes.

Conclusions

We are demonstrating the use of heterogeneous and electrochemical catalysis for production of chemicals and fuels from renewable cellulosic biomass. Pt/Vulcan has showed better oxidation of HMF into FDCA in highly basic condition (pH 13), with 80% FDCA yield than pH 10 conditions. The reaction kinetics showed that the oxidative pathway starts with the fast oxidation of HMF into FDC, hemiacetal than to FFCA and the limiting reaction step is the oxidation of FFCA into FDCA. In case of electrocatalysis, the yield and selectivity of desired products are low because of less active surface area of electrode when compared to high surface area Pt/Vulcan. Further research is under progress to increase the yields of desired products by increasing the surface area of electro-catalyst.

References

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Fig. 4. Cyclic Voltammogram of Pt foil (4.5 cm²)_{geo} at a scan rate of 50 mV/s in 5mM HMF with 0.1M H₂SO₄ supporting electrolyte, pH 1.2.

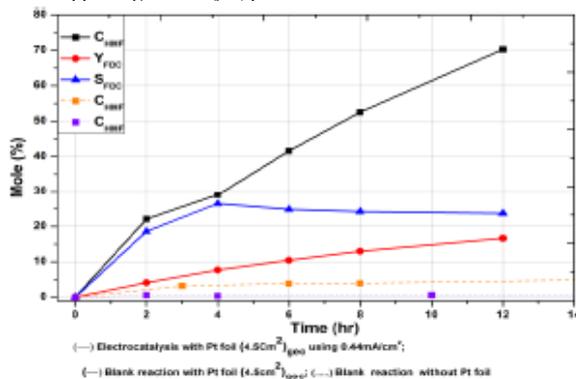


Fig. 5. Anodic oxidation of 5mM HMF using Ni foil (4.5 cm²)_{geo} at 0.44mA/cm² current density, 25°C under N₂.

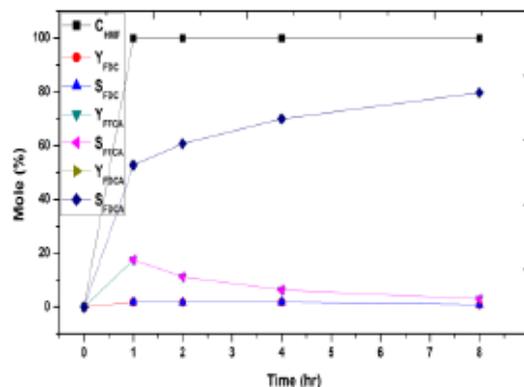


Fig. 6. Oxidation of 5mM HMF using 25mg of 20% Pt/Vulcan at 10bar of O₂ and 50°C in pH13 (0.1M NaOH).

