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Simultaneous dehydration of biomass-derived sugars to 5-hydroxymethyl furfural (HMF) and reduction of graphene oxide in ethyl lactate: one pot dual chemistry†

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Low yield of chemicals is often identified as a major obstacle for the complete utilization of bioresources as a source of important chemicals and thereby limits their application in industries. The issue of low yield can be partially compensated by integrated processes, *i.e.*, production of two or more chemicals from the same biomass using single or multistep processes. Herein, a simple pathway for simultaneous production of 5-hydroxymethyl furfural (HMF) from biomass-derived sugars by dehydration of fructose (molar yield 76.3%) using graphene oxide (GO) as acid catalyst and choline chloride (ChoCl) as additive in ethyl lactate is demonstrated. Moreover, during the course of reaction GO was reduced to produce six-layered graphene nanosheets (96% recovery). Furthermore, the solvent was recycled after recovery of both products and successfully reused for subsequent production of the two chemicals with high purity.

Introduction

Biomass is considered the most appropriate sustainable resource for the production of biofuels as alternative to existing fuels derived from fossil resources. Research has geared up recently due to the gradual dwindling of fossil resources. It is proposed that 18% of total manufactured chemicals will be sourced from biomass by 2020.[1] Although there are plenty of reports available in the literature on conversion of biomass to ethanol or other valuable chemicals,[2] special attention has been focused on 5-hydroxymethylfurfural (HMF), which is the dehydrated product of simple sugars and is the precursor of the superior biofuel, 2,5-dimethylfuran (DMF).[3–5] Usually, HMF is prepared from fructose, glucose, sucrose, cellulose and inulin.[3] In this line of research, we have recently demonstrated *Kappaphycus alvarezii*, a red seaweed, as an effective alternative precursor for the production of HMF along with potassic fertilizer, levulinic acid, formic acid and pure water.[5] HMF is considered an important platform chemical, required in different biorefinery processes to derive various important chemicals as shown in Scheme S1 (ESI†).[2] Although several routes for the synthesis of HMF are reported in the literature, including processes using ionic liquids and other solid acid catalysts,[6,7] there are only few reports available on using bio-based catalyst for such syntheses. Recently, it was reported that HMF could be produced with a maximum yield of 84% using choline chloride (ChoCl)/betaine hydrochloride (BHC)/water system at 110 °C under heating for 1 h.[8] Use of ChoCl–H_2O/MIBK (methyl isobutyl ketone) biphasic system in the presence of $AlCl_3$ catalyst at 165 °C under microwave condition for 15 minute produced HMF with 70% yield.[9,10]

Carbon-based materials such as carbon nanotubes and graphene oxide (GO) have been explored as green catalysts for a number of sustainable chemical transformations.[11,12] GO was reported as an efficient catalyst for dehydration of fructose to HMF (31% yield) at 100 °C for 24 h.[13] The produced HMF was further reacted with ethanol to yield ethoxymethyl furfural but the fate of GO was not discussed, *i.e.*, whether GO was reduced during the reaction was not investigated.[13]

While HMF is no doubt of great importance, it is of immense interest that the economics of renewable bioresources can be made more attractive through integration with the conformation of other essential products having practical commercial applications.[14] Carbon-based nano materials, especially graphene, is going to play a very vital role in the development of new materials in the future. Graphene consists of 2D sheet-like structure with "honeycomb" decoration and made up of conjugated sp^2 carbon.[15] Graphene is used extensively for

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