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Fabrication of furfural and hydroxymethylfurfural from carbohydrates by heterogeneous catalysis: A review

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Abstract

Furfural and 5-hydroxymethylfurfural (5-HMF) have been recognized as valuable biomass-derived platform chemicals and bridges between biomass raw materials and the biorefinery industry, utilizing as a building-blocks for the production of many chemicals and fuels. Biorefinery refers to a facility that integrates biomass conversion to produce fuels, power, heat and value-added chemicals from biomass. The biorefinery concept is thus analogous to today's petroleum refinery which produces multiple fuels and products from oil. Furfurals are important intermediates in the chemical industry. They are produced by homogeneous catalysis in an aqueous solution. The elimination of homogeneous mineral acids makes the reaction mixtures less corrosive, produces less waste and facilitates easy separation and recovery of the catalyst. Furfural is produced in the dehydration of xylose and HMF is formed from glucose and fructose. They are formed only in the presence of an acidic catalyst. Bases are not active in dehydration reactions but do catalyze the isomerization of monosaccharides which are favourable when using glucose as a raw material. Lignocellulosic biomass, a cheap and plentiful resource could play a key role in the production of sustainable chemicals. The simple sugar contained in the renewable lignocellulosic biomass can be converted into commercially valuable products such as 5-hydroxymethylfurfural (5-HMF). Finding an active and stable water-tolerant solid acid catalyst still poses a challenge for the production of furfural (furan-2-carbaldehyde) and 5-(hydroxymethyl)-2-furaldehyde (5-HMF). This review summarizes catalytic conversion approaches, focusing on the heterogeneously catalyzed formation of furfural. The attractiveness of catalytic concepts is evaluated, keeping in mind productivity, sustainability and environmental footprint. The study is targeted at gaining an understanding of the key aspects of catalyst design and development for sugar chemistry and therefore attention is also given to heterogeneous catalysis related to HMF.

Keywords: Glucose, fructose, HMF, catalysis

Introduction

Biorefining in the forest industry is based on the removal of biomass constituents that do not contribute to the paper and cellulose products. Hemicelluloses could be removed by autohydrolysis or alkaline extraction of the wood prior to kraft-pulping. In addition to kraft-pulping, pulping process include mechanical pulping, non-wood pulping, semichemical pulping and sulphite pulping all of which are much less common. In Brazil, sugarcane bagasse offers an excellent feedstock for the production of cellulosic ethanol or chemicals. The valorization of sugarcane bagasse by extracting xylose has also gained attention. Lignocellulosic biomass is without any doubt a valuable raw material source with varying proportions of lignin, hemicellulose and cellulose. Glucose and xylose degradation product that results from the pretreatment of pulp and paper industry, involving acids at elevated temperature, typically include HMF and Furfural which can be used to produce levulinic and formic acid. The potential of Furfural and HMF derivatives in traffic fuel applications has recently been highlighted by James *et al.* The development of low cost processes for the manufacture of both furfural and HMF and further development of related new intermediated

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and products, relies on emerging catalytic process concepts. The traditional process are based on homogeneous acid catalysts such as sulphuric acid. These homogeneous catalysts are corrosive and pose environmental risks. Heterogeneous catalysts would be safer and more environmentally friendly in accordance with the principle of green chemistry.

Production of furfural and HMF

The first commercial process for the production of furfural was started by Quaker Oats in 1921. Over the global 70% of the furfural production is located in PR China. In 2005, the total global production globally was Ca 280000 tones per year, out of which PR China produced 200000 tones. Currently, most furfural is produced by PR China using the Westpro-Modified Huaxia Technology used in PR China. The traditional processes are based on homogeneous acid catalysts such as sulphuric acid. So far, in spite of the active research on heterogeneous catalysts in furfural production, the commercial production of furfural still is based on the use of homogeneous acids as catalysts.

Xylose to Furfural

Furfural (furan-2-carbaldehyde) is typically produced in the dehydration of xylose in the presence of an acidic catalyst. Depending on temperature and reaction time, the conversion of xylose can reach, 26% after 4 h in 160°C and 84% after 24 h in 140°C, while the selectivity to furfural remains low (8% and 27%, respectively). In addition to dehydration, several other reactions takes place. The monosaccharides are isomerized, that is, xylose reacts to lyxose and xylulose. At low temperature of 140-160°C, lyxose is more prominent than xylose. The reaction of xylose to lyxose and to furfural is rapid at ca. 200°C. Fragmentation products of furfural include formaldehyde, formic acid, acetaldehyde, crotonaldehyde, lactic acid, dihydroxyacetone, glyceraldehyde, pyruvaldehyde, acetol and glycolaldehyde.

Glucose to HMF

HMF (5-(hydroxymethyl)-2-formaldehyde) is formed from glucose and fructose. The production of HMF is interconnected to that of furfural because HMF is also formed from furfural under conditions in which dehydration of monosaccharides proceeds. The formation of HMF from fructose is faster than from glucose because the ring structure of glucose is more stable than the ring of fructose. Similarly to furfural, HMF can also be formed via a non-catalytic reaction.

Heterogeneously Catalyzed Approaches

The dehydration of monosaccharides is catalyzed by acids and a large variety of heterogeneous catalysts with acidic character has been studied. These include zeolites, heteropolyacids, sulfated zirconias, ion-exchange resins and solid metal phosphates. Considering the use of supports, it should be noted that alumina or silica supports do not possess catalytic activity in the dehydration of monosaccharides. On the other hand, basic materials are not active in the dehydration reaction either, while they do catalyze the isomerization of monosaccharides.

Conclusion

The development of low-cost processes for the manufacture of both furfural and HMF and further development of

related new intermediates and products, relies on the development of new economically viable catalytic process concepts. The evolution of heterogeneously catalyzed production efforts towards furfural and HMF indicated that both the pore structure and acidity of the catalysts affect activity in the dehydration of monosaccharides. Although basic materials are not active in dehydration reaction. Glucose, a cheap raw material can be isomerized to fructose which has the higher rate in the dehydration reaction. Water is the most economical and environmentally friendly solvent to be used in the reactions of monosaccharides. Out of zeolites, mordenite has been active for the dehydration reaction particularly in connection with the use of organic solvents. Ion-exchange resins and modified zirconias are also suitable catalysts for the production of furfural. Further development and optimization of the catalysts and the reaction setup are still needed to facilitate the commercial production of furfural with heterogeneous catalysts.

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