

Aerobic oxidation of HMF to FDA with ruthenium containing ferrite-spinel catalyst

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Introduction

In the past years, there has been a rising demand for efficient heterogeneously catalysed oxidations of e.g. alcohols and aldehydes, for production of both fine and bulk chemicals [1]. So far, these industrially important oxidations have often been carried out using stoichiometric amounts of high-valent inorganic reagents, such as chromate or permanganate, which unfortunately leads to the generation of large amounts of metal waste [2].

In order to avoid waste generation, considerable effort has been put into the development of aerobic oxidation methods using molecular oxygen as the stoichiometric reagent. These methods represent an interesting and highly atom-efficient alternative, as oxygen is cheap, readily available, and an oxidant that produces water as the only by-product. Efficient aerobic oxidation is, however, strongly dependent on a good heterogeneous catalyst which facilitates efficient oxygen activation. The most common catalysts which have been applied for transformations involving aerobic oxidation are based on expensive precious metals like, e.g. Au, Pt and Pd [3,4]. Recent studies have shown that ruthenium oxides are active oxidation catalysts for various functional groups and biomass derived compounds [5,6], although most reports of ruthenium-based aerobic oxidations are limited to alcohol oxidations in organic solvents. As ruthenium is considerably less expensive than the previously mentioned metals, it is more feasible to use Ru in catalysts for industrial applications.

An interesting biomass derived compound is 5-hydroxymethyl furfural (HMF) which is produced from glucose or fructose. HMF can be oxidized into a wide variety of compounds, where 2,5-furandicarboxylic acid (FDA) and levulinic acid have been defined by the US Department of Energy biomass program as two of the twelve chemicals obtained from biomass that can be used as chemical building blocks in the future [7]. Due to its resemblance to terephthalic acid, FDA has been promoted as a renewable building block for production of plastics.

In this work we have used a ferrite-spinel based catalyst, $\text{Fe}_{1.5}\text{Ru}_{0.35}\text{Cu}_{0.15}\text{O}_4$, previously described by Kaneda et al. [8] to efficiently oxidize HMF to FDA in water in the presence of molecular oxygen. The effect of temperature and pressure on the reaction will be discussed,

along with results obtained when altering the metal content or depositing the catalyst on support.

Experimental

The catalyst was prepared using a method previously described by Kaneda et al. [8]. HMF oxidations were carried out in water in a stirred autoclave pressurized with oxygen and equipped with internal thermocontrol. Catalyst loading, reaction times, temperature and pressure were varied between experiments. The degree of conversion and yields of individual products were quantified by HPLC.

Results/Discussion

Results show quantitative conversion of HMF and 56% yield of FDA, after 6 hours of reaction at 10 bar O_2 and 110°C, using a molar ratio Ru to HMF of 0.2. Above 90% yield of FDA can be achieved in 21 hours under the same reaction conditions. The transformation of HMF to FDA is believed to proceed mainly via the intermediate 5-hydroxymethyl-2-furancarboxylic acid, and to a lesser extent via 2,5-furandicarbaldehyde.

Preliminary studies show that increased temperature and pressure affect the reaction rate in a positive way resulting in higher yields of FDA.

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