Precious metals for green chemistry

Gisa Meissner and Konrad Krois,
Heraeus Deutschland GmbH & Co. KG, Germany, discuss the use of precious metal-based catalysts for the efficient conversion of 5-hydroxymethyl furfural (5-HMF) into 2,5-diformylfuran (DFF) to produce phenolic resins.

The negative impacts of greenhouse gases such as carbon dioxide (CO_2) are widely recognised as complex challenges. It is essential to move away from our dependence on petroleum-based products, from both an environmental and economic perspective. Although petrochemicals are the predominant feedstock in the chemical industry, the utilisation of renewable feedstocks to produce chemicals is taking off, with the aim of reducing carbon footprint in order for various base chemicals to have a positive environmental impact.[1] As such, it is important to seek alternative platform base chemicals that are based on sustainable green chemistry in order to support the manufacture of the important products used in our daily lives.

Aside from the option of finding drop-in solutions to existing fossil-based platform chemicals, the switch towards renewable feedstocks allows for – and sometimes even mandates – entirely new and different process routes. Consequently, this leads to chemicals with new functionalities and properties that previously had no economic pathway, allowing for further value creation. Whereas many renewable feedstock-based chemicals are derived from the use of biochemical routes, traditional chemical catalysis and processes

Figure 1. 5%Ru/Al_2O_3 catalyst for the effective conversion of 5-HMF in DFF.

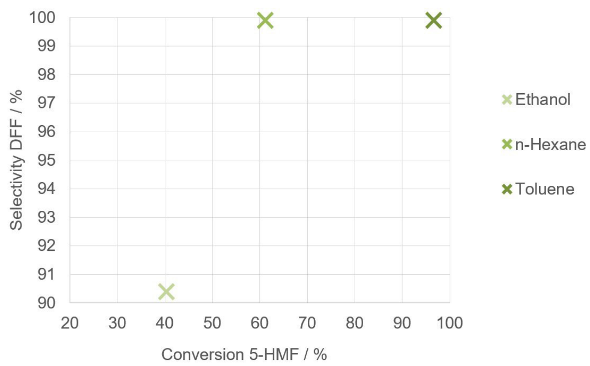

Figure 2. Solvent-screening results for the oxidation of 5-HMF into DFF using a 3%Ru/Al_2O_3 catalyst with molecular oxygen, after 3 hr reaction time.

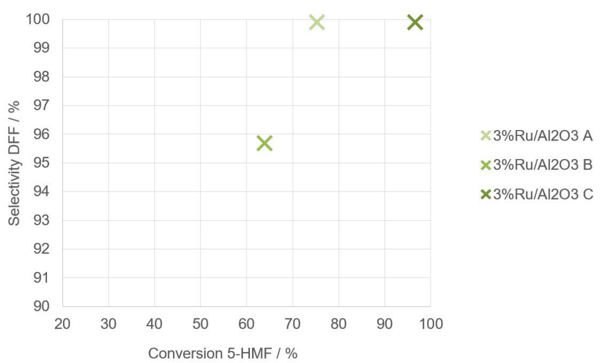

Figure 3. Results of the support influence for the oxidation of 5-HMF into DFF using different 3%Ru/Al_2O_3 catalysts with molecular oxygen in toluene, after 3 hr reaction time.

remain a cornerstone for the conversion of renewable feedstocks. At present, more than 80% of processes deployed on an industrial scale use different catalysts for the synthesis of a variety of chemical, petrochemical and biochemical products, as well as polymers.[2] According to the 12 principles of green chemistry, selectivity, efficiency and sustainability play a pivotal role in chemical processes as a whole.[3] Chemical intermediates based on renewable feedstocks can be properly integrated into the traditional chemical industry by using heterogeneous precious metal-based catalysts, and these also align with the principles of green chemistry.[4, 5]

The paradigm shift towards, and market demand for, renewable feedstocks in the chemical industry was recognised by Heraeus several years ago, initiating a development programme for precious metal-based catalysts targeting the conversion of various renewable feedstocks such as biomass, CO_2 or waste plastics into value-added, sustainable chemicals (Figure 1). Generally, these chemicals, derived from renewable feedstocks such as biomass i.e. sugarcane, harvest or wood residues, have a significantly smaller carbon footprint and have a better life cycle assessment compared to their fossil-based counterparts. Forestry residues, such as lignin or 5-hydroxymethyl furfural (HMF) from cellulose, can serve as a renewable source for value-added chemicals.[6, 7]

One such platform can be 2,5-diformylfuran (DFF), which is a highly-flexible chemical that can be used for a variety of bio-based products, such as plastic bottles, where it replaces terephthalic acid after a catalytic oxidation step. Additionally, polyamides, polyurethanes and many other products can be derived from this platform chemical. In particular, DFF facilitates the production of formaldehyde-free phenolic resins as glue for chipboards in the furniture industry, for example.

This article focuses on the development of efficient oxidation of 5-HMF into DFF. The use of heterogeneous Ru/Al_2O_3 catalysts leads to the complete conversion of 5-HMF, as well as the selective formation of DFF with molecular oxygen. Both ruthenium loading and the selected support material influence the catalyst performance. Furthermore, the recovery and recycling of ruthenium as precious metal is of great importance from an ecological and economical point of view. The next section will highlight strategies to obtain organic building blocks and platform chemicals from renewable feedstocks by the effective deployment of precious metal-based catalysts. It will also discuss the cost attractiveness of precious metal-based catalysts, when applying recycling loop strategies, which allow for the efficient use of the scarce precious metals.

Precious-metal catalysts for the efficient conversion of 5-HMF

Heraeus is actively developing and optimising catalysts for conversion processes of renewable feedstocks, together with partners from industry and academia. The Competence Centers for Excellent Technologies (Comet), a technology cooperation programme founded by the Austrian government, focuses on the valorisation of organic materials and total biomass utilisation into sustainable products and energy.

Native biopolymers from woody biomass are separated to obtain 5-HMF from cellulose as a starting material for DFF for bio-based products, such as phenolic resins with a substitution of formaldehyde. Heraeus developed a new ruthenium-based catalyst for the efficient formation of DFF from 5-HMF as an important bio-based platform chemical. The heterogeneous catalytic oxidation of 5-HMF with molecular oxygen leads to the selective formation of DFF.

Different solvents were tested using a 3%Ru/Al_2O_3 catalyst prior to the catalyst screening (see Figure 2). In comparison to polar protic solvents, such as water or ethanol, a total selectivity towards DFF was found for non-polar solvents, such as hexane and toluene. Since toluene not only produced the highest DFF selectivity, but also a full HMF conversion, it was chosen as the most suitable solvent for further investigations.

The catalyst performance not only depends on the solvent chosen, but also on the precious metal precursor solutions that are used, e.g. ruthenium chloride or ruthenium nitrosyl nitrate, as well as on the intrinsic characteristics of the support. To investigate the influence of the support, three 3%Ru/Al_2O_3 catalysts (A, B and C) were tested on different alumina supports (see Figure 3). The highest HMF conversion of 97% with a DFF selectivity of 99.9% was obtained using an alumina support with a BET area of 155 m^2/g (ruthenium catalyst C). This support lead to a reaction rate that was almost twice in comparison to the other catalysts.

It is noteworthy that no 5-formyl-2-furancarboxylic acid (FFCA), 5-hydroxymethyl-2 furancarboxylic acid (HMFCA) or 2,5-furandicarboxylic acid (FDCA) were detected as over-oxidation products with these Ru/Al_2O_3 catalysts.

Following this, Heraeus investigated the influence of the ruthenium loading of catalyst C. Interestingly, the higher the ruthenium loading of the catalyst, the higher the catalyst activity towards the formation of DFF (see Figure 4). Without ruthenium, the activity is very low, with only 0.1 mol (HMF) mol $(Ru)^{-1}$ h^{-1}. In contrast, activity of 18 mol (HMF) mol $(Ru)^{-1}$ h^{-1} is observed, with a loading of 3% ruthenium. This was improved, and a 5% ruthenium loading lead to an activity of 28 mol (HMF) mol $(Ru)^{-1}$ h^{-1}.

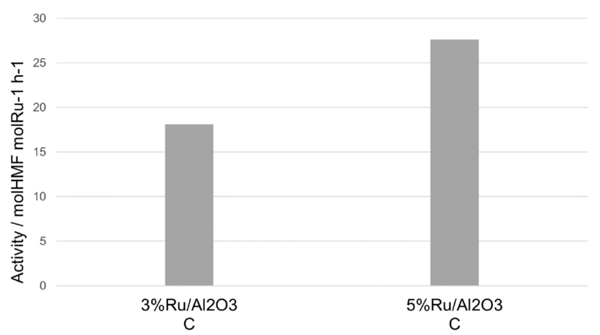

Figure 4. Results of the ruthenium loading influence for the oxidation of 5-HMF into DFF, using a 3%Ru/Al_2O_3 and 5%Ru/Al_2O_3 catalysts with molecular oxygen in toluene, after 3 hr reaction time.

After washing, this 5%Ru/Al_2O_3 catalyst can be reused several times. Nevertheless, after the catalyst is deactivated, the precious metals recovery plays a key role from both an ecological and economical point of view. The full 'precious metal loop' offered by Heraeus consists of the precious metal winning, the production of precious metal solutions, as well as the catalyst synthesis, followed by its performance as an active catalyst. Finally, the deactivated catalyst is separated from the reaction mixture to close the loop with the precious metal recycling, which again serves as a precious metal source. This catalyst recycling is not only cost competitive, but also ecological. The recycled secondary precious metal can reduce the carbon footprint by up to 98% in comparison to primary precious metal from mining.

Conclusion

DFF is a promising platform chemical derived from renewable feedstocks from which a variety of bio-based products can be manufactured. Heraeus has therefore developed an efficient catalyst for the oxidation of 5-HMF to DFF. The use of a heterogeneous Ru/Al_2O_3 catalyst with an optimised choice of precious metal precursor and support material leads to a large increase in activity relative to a non-optimised catalyst. A complete conversion of 5-HMF and the selective formation of DFF without the formation of the over-oxidation products, HMFCA or FDCA, is possible. Furthermore, the activity could be further optimised by increasing the ruthenium loading of the catalyst by up to 5%. Heraeus offers a comprehensive product and service portfolio along the precious metals value chain – from catalysts to recycling.

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Note

The authors would like to thank Birgit Kamm and Christoph Derflinger for their work on the project 'Wood K plus Comet Funding Period 2019 – 2022', funded by the Austrian Research Funding Association (FFG).