Industry Perspective

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Black Powder for Green Chemicals: Heraeus Precious Metal-based Catalysts for the Efficient Conversion of Lignin into Phenolic Resins

By Gisa Meissner, PhD

Introduction

The negative impact of greenhouse gas emissions and global warming is widely recognized by society, politics, academia, and industry as a major and complex challenge for this decade and the decades to come. Although fossil feedstock was and is the predominant feedstock for the chemical industry, the use of biomass as renewable feedstock to produce chemicals is taking off the ground, targeting a reduced CO_2 footprint for various base chemicals (Li, et al., 2015). For aromatics and furfural-type chemistry lignin-based feedstock has recently gained interest (Suess, et al., 2021; Pineda and Lee, 2016). This article reports on the progress made with precious metal (PM) based catalysts ("black powder") to extract value added chemicals such as phenol and hydroxymethyl furfural (HMF) ("green chemicals") from lignin-containing forestry residues.

The use of Platinum-based catalysts ensures the access to important organic building blocks as sustainable products made from lignin. The complete avoidance of any coke formation allows the application of the obtained phenolics as starting material for phenolic resins. The PM recovery allows an efficient use of scarce raw materials such as Platinum and improves the competitiveness to non-precious metal-based alternatives.

Significance

The search for renewable feedstock in the chemical industry has been recognized by Heraeus several years ago, initiating a development program for precious metal based catalysts for different processes targeting the conversion of various biomass feedstocks into value added biobased chemicals. Generally, biobased chemicals are derived from renewable feedstocks such as sugarcane, harvest- or wood-residues and often show a more attractive carbon footprint or life cycle analysis compared to their petro-based analogues. However, besides the opportunity of finding biobased drop-in solutions, new functionalities can sometimes be generated, when shifting to the novel feedstocks and processes, allowing for further value creation. Whereas many biobased chemicals are derived using biochemical routes, traditional chemical catalysis and process routes remain an important element for the conversion of biomass feedstock. Biomass-based intermediates can be properly integrated in the traditional chemical industry using heterogeneous PM catalysts. (Pineda and Lee, 2021; Kohli, et al., 2019).

Heraeus is actively developing and optimizing catalysts for such conversion processes, very often together with partners or process owners, as well as highlighting strategies to obtain organic building blocks from biomass using precious metal-based catalysts and shows the cost attractiveness of precious metal-based catalysts, when applying recycling loop strategies, which allow an efficient use of the scarce PMs.

More than 80% of present industrial processes use different catalysts for the synthesis of a variety of chemical, petrochemical, and biochemical products as well as polymers (Deutschmann, et al., 2000). According to the twelve principles of green chemistry, selectivity, efficiency, and sustainability play a pivotal role (Poliakoff and Licence, 2007).

The Competence Centers for Excellent Technologies (Comet), a technology cooperation program founded by the Austrian Government, focuses on the valorization of organic materials and the total biomass utilization into sustainable products and energy. Native biopolymers from woody biomass are separated to obtain lignin as starting material for bio-based products, like resins.

Catalysts for Efficient Lignin Conversion

Platinum-based catalysts are applied for the efficient formation of phenolics from lignin for the use in phenolic resins. The catalyst performance depends on the used precious metal precursor solutions, e.g., Platinum nitrate, hexachloroplatinic acid or Platinum oxalate and on intrinsic characteristics of the support. Specifically, the special nature of a hydrotalcite (HTC) as support material shows positive effects on the catalyst performance. An HTC based Platinum catalyst leads to much better lignin conversions in comparison to the HTC support itself (**Figure 1**).

The higher the Platinum-loading of the catalyst, the higher the preference towards the formation of monomeric and oligomeric structures. The addition of 1% Nickel strengthens this effect with a decreased coke formation. (**Figure 1**). A higher Platinum loading leads to a full lignin conversion, which can be explained by an increased PM surface area (**Figure 2**). A higher PM surface area

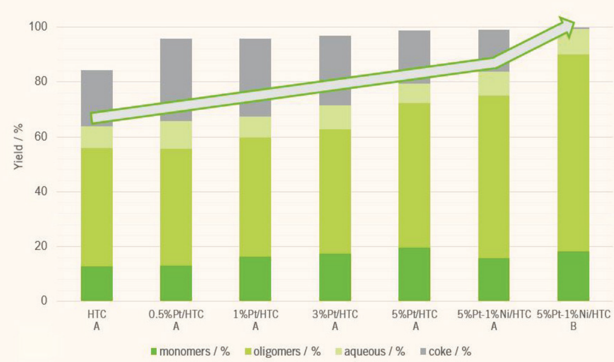

Figure 1. Results of the lignin conversion using five different Platinum-based catalysts under standard reaction conditions (A) and optimized reaction conditions (B) after DoE (design of experiments) evaluations.

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New, Highly Efficient Catalyst for Propylene Production

Researchers have developed an innovative catalyst for the synthesis of propylene, which has potential benefits for the chemical industry and carbon recycling. Researchers at Hokkaido University have developed an innovative catalyst for the production of propylene that is highly active, selective, stable and utilizes carbon dioxide (CO_2) efficiently. Hokkaido University molecular engineer, Shinya Furukawa and his colleagues developed a catalyst made from three different metals (platinum, cobalt and indium), each chosen for its specific properties. Platinum was selected as the main active metal because of its ability to break chemical bonds between carbon and hydrogen, enabling the dehydrogenation reaction. Cobalt accelerates CO_2 capture and activation, while indium enhances the catalyst's selectivity. The metals were fixed to a support made from cerium oxide. The researchers tested the catalyst's activity at 550°C and compared the results with existing catalysts. They also performed a mechanistic study to understand the functions of the different components and found the catalyst links the propylene-forming reaction to the deoxygenation of CO_2, and ensures the catalytic activity is specific to propane; water and carbon oxides are formed as byproducts. Further, they found that the catalyst increased the reaction rate approximately five fold compared to the typical values reported from other systems. The reaction produced a higher ratio of propylene and utilized more CO_2 at 550°C compared to previous catalysts. The catalyst also showed good long-term stability and reusability. This study provides new insights into the design of highly efficient catalysts for petrochemical production, and has potential benefits for carbon recycling and greenhouse gas reduction. Source: Science Daily, 1/27/2022.

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indicates smaller Platinum particles on the HTC surface, resulting in a higher catalyst activity. Although a lower PM surface area was observed for the 5%Pt-1%Ni/HTC catalyst, the Nickel addition improves the formation of oligomeric phenolic structures. Afterwards, the reaction conditions were optimized based on a design of experiments (DoE) with the successful avoidance of any coke formation using 5%Pt-1%Ni/HTC as catalyst.

The recovery of precious metals (PM) plays a key role from both an ecological and economical point of view. The full "PM loop" consists of the PM winning and PM solution production as well as the catalyst synthesis, followed by the performance as active catalyst. Finally, the deactivated catalyst is separated from the reaction mixture to close the loop with the PM recycling, which serves again as PM source. Like for traditional petrochemicals, catalysts and especially precious metal catalysts can play a critical role to transform different feedstocks into valuable chemicals economically. Furthermore, catalyst recycling helps with cost-competitiveness.

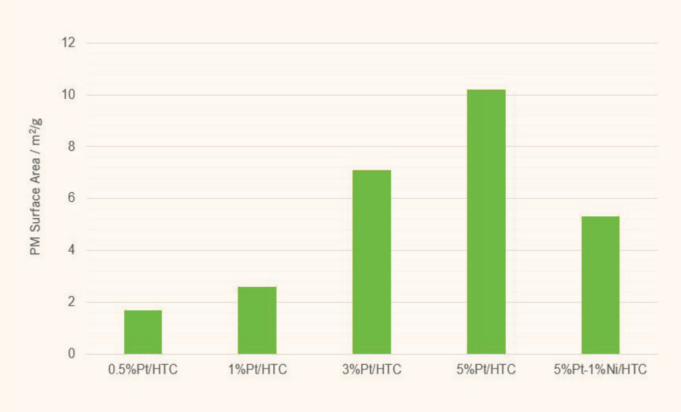

Figure 2. PM surface area of HTC-supported Platinum catalysts based on carbon monoxide adsorption.

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About the Author

Gisa Meissner did her PhD in inorganic and fluorine chemistry at the Humboldt University Berlin. After a Post-doc, she joined Heraeus Precious Metals as a project leader in the R&D department for Chemical Catalysts in 2018 and is responsible for the development of new heterogeneous catalysts. Gisa can be reached at gisa.meissner@heraeus.com.