# Precious metal based microsphere catalysts to bridge the gap between **batch & continuous processes**

**Franziska Heck** and **Artur Gantarev** of **Heraeus Precious Metals** discuss the development of precious metal-based carbon microspheres catalysts for the pharma industry

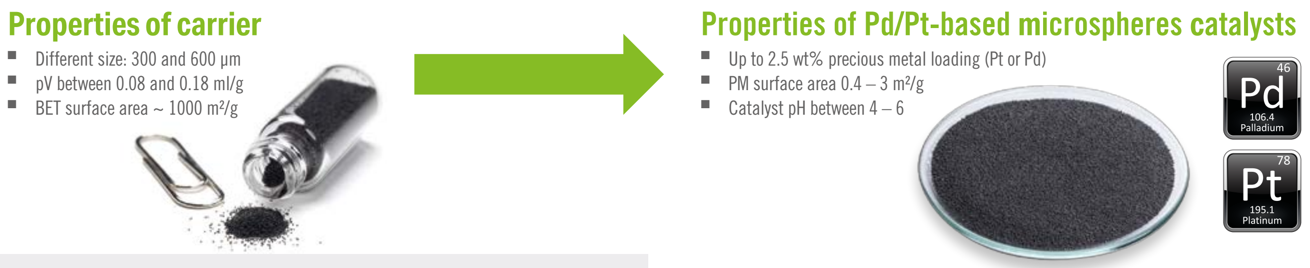


Figure 1 - Properties of carbon carrier & Pd-/Pt-based microsphere catalysts

Process efficiency and productivity have always played a major role in the development and optimisation of chemical production processes. Furthermore, producers are seeking to minimise the impact on the environment, such as through the reduction of harmful (greenhouse) gas emissions. In addition to the preferred use of abundant, renewable resources, process optimisation itself has great potential for the establishment of 'greener' solutions.

Among the Twelve Principles of Green Chemistry, atom economy and selective catalysis point to the importance of process efficiency.[1,2] In particular, the role of catalysis is critical, as more than 80% of today's industrial processes for the synthesis of bulk chemicals, fine chemicals, agrochemicals and pharmaceuticals rely on the efficient use of catalysts.[3] Therefore, making the right choice for this 'heart of the process' is essential.

To make chemical processes more efficient and thus greener, the right catalyst has to be selected in combination with the right reactor type. Particularly in pharmaceutical production (such as for manufacturing small molecules and APIs), many processes are established in batch mode, typically using powder-based catalysts.

However, the pharmaceutical industry is also increasingly focused on process improvement and is undergoing a transformation toward continuous processes that require shaped catalysts.[4] Consequently, it is slowly moving away from the use of traditional powder-based catalysts.

This transition offers significant advantages, including favourable catalytic properties, improved selectivity, reduced catalyst losses and easier scalability. By leveraging these benefits, pharmaceutical manufacturers can optimise their production processes, resulting in improved product quality, and increased operational efficiency and cost-effectiveness.

To bridge this transition, Heraeus is developing precious metal-coated carbon microsphere catalysts, a type of heterogeneous catalyst that can be used in both batch- and continuous-operated reactors. This also provides a better foundation for comparing both operation modes.

## Significance

Continuously operated processes allow precise control of reaction parameters, resulting in consistent and high-quality products. This is particularly important in the pharmaceutical industry, where more and more processes are being transferred from batch to continuous mode.

One way to bridge this transition is to use suitable shaped catalysts that are applicable in both batch and continuous mode. This can be achieved by using chemically and mechanically robust microsphere carriers coated with precious metals as a direct replacement for powder-based catalysts. The catalysts presented here expand the boundaries of conventional precious metal-based catalysts and combine advantages of powder and shaped catalysts. Due to their small particle size compared to conventional shaped alumina or carbon catalysts, they can easily be deployed in small-scale set-ups and microreactors.

Moreover, their advantageous physical properties, such as narrow particle size distribution, high specific surface area and pore volume in combination with a high crushing strength, allow them to be used even under harsh reaction conditions in fixed bed- and batch-operated reactors.

Continuous flow hydrogenation reactions are of particular interest for many industrial players. Heraeus is actively developing and optimising catalysts for such processes, often in cooperation with partners and process owners. The company is also mapping out strategies to obtain value-added products by using precious metal-based catalysts, while demonstrating cost attractiveness and sustainability responsibility by applying recycling strategies to keep the once-mined scarce precious metal 'in the loop'.

Herein, we present newly developed platinum- and palladium-based catalysts on carbon microsphere supports. Figure 1 illustrates the core properties of carbon microspheres and the corresponding precious metal catalysts.

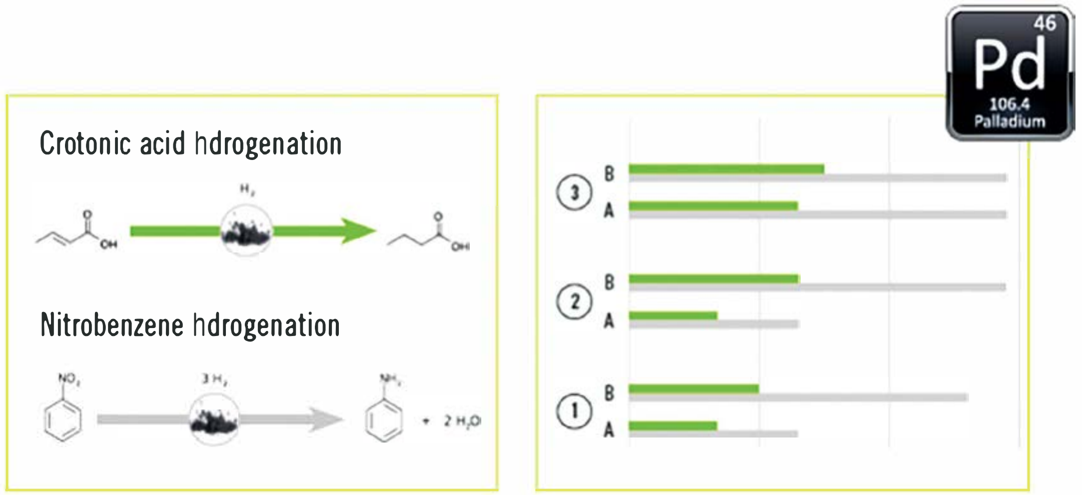


Figure 2 – Effects of varying preparation parameters on hydrogenation activity

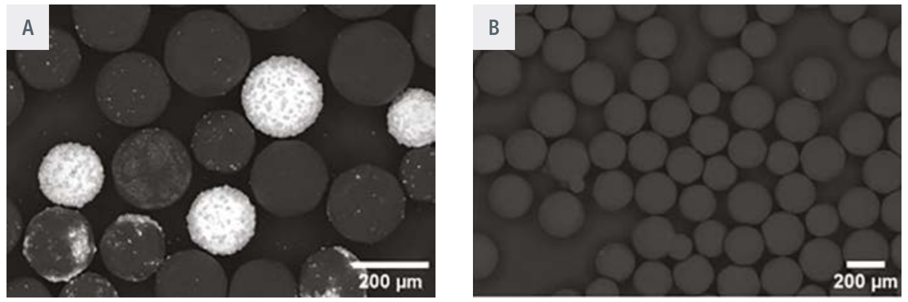


Figure 3 – SEM image of 2.5 wt% Pd/C carbon microspheres with precursors A (left) & B (right)

## Results & discussion

The main goal of systematically optimising the preparation conditions was to achieve a homogeneous distribution of the precious metal on the catalyst support and ensure a high level of activity in hydrogenation test reactions.

Hydrogenation test reactions of nitrobenzene and crotonic acid were conducted to determine the catalytic activity, while scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) analyses were used to assess the homogeneous distribution of the precious metal on the support.

The optimisation of the catalyst preparation procedure included three distinct stages. First, the impact of pre-treatment on the catalyst activity was investigated. Two different pre-treatment procedures were applied to the support before loading the microspheres with precious metal.

By switching to more suitable conditions a significant increase in activity in the hydrogenation of nitrobenzene could be observed (Figure 2). Subsequently, the variation of precious metal precursor solutions was studied, which led to a conversion increase of approximately 50% in the hydrogenation of nitrobenzene.

The dispersion of the precious metal with precursor A resulted in a very non-homogeneous distribution of the active phase (Figure 3). Significant improvement was achieved by using precursor B and a considerably more homogenous distribution of precious metal on the carrier could be achieved.

Quantitative determination of the palladium content of different catalysts particles by SEM-EDX analyses further supports the impression that palladium is homogeneously dispersed when precursor B is used. Palladium content prepared with precursor B was determined by SEM-EDX to be 2.33%, 2.51% and 2.44% at three selected points.

Lastly, various reducing agents were tested to evaluate their influence on the hydrogenation activity and palladium distribution. Finding the right reducing agent and reduction procedure is crucial to not only ensure complete reduction of the noble metal but also to prevent agglomeration of the active phase. Reducing agent A led to a slightly lower activity in crotonic acid conversion, whereas using reducing agent B led to a 15% increase in nitrobenzene conversion.

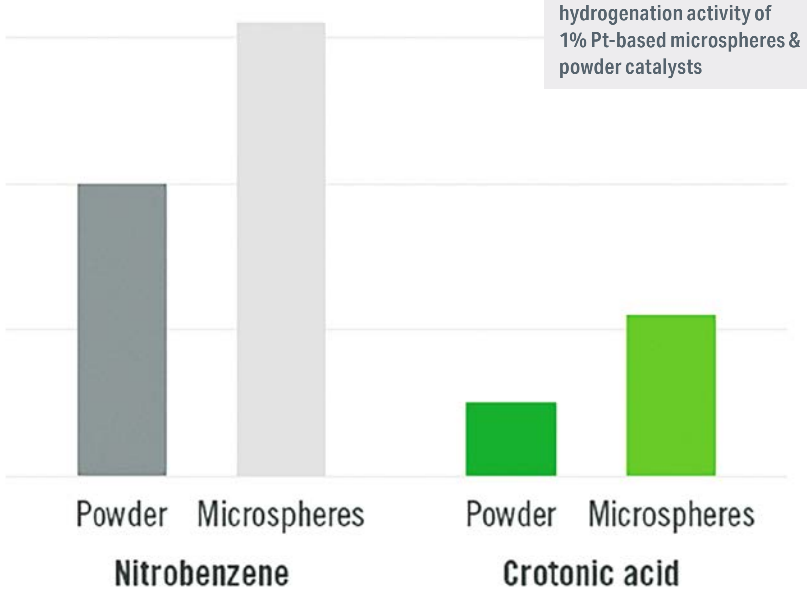


Figure 4 - Comparison of hydrogenation activity of 1% Pt-based microspheres & powder catalysts

## Comparisons of results

Beside the previously discussed palladium-containing catalysts, platinum-coated microsphere catalysts were prepared using an analogous, optimised synthesis route. Both metals are highly catalytically active in hydrogenation reactions.

There were differences in their respective performances, with platinum microspheres displaying higher activity for nitrobenzene hydrogenation and palladium microspheres showing higher activity for crotonic acid hydrogenation. This trend is similar to the behaviour of our standard carbon powder-supported catalysts.

To compare the novel microsphere catalysts with conventional powder catalysts, two catalysts with the same precious metal loading (1 wt% platinum) were prepared using carbon powder as well as a microsphere carrier. With a BET surface area of 1,230 and 1,330 m²/g, the surface area for both types is quite similar.

By using platinum-loaded microspheres catalysts an improvement in hydrogenation reactivity for both test reactions was achieved. (Figure 4) We believe that a smaller particle size of the active phase on the catalyst surface is the reason for the improved conversion rate with the microsphere catalysts. Further investigations to prove this hypothesis are ongoing.

## Conclusion

This investigation presented the successful development of platinum- and palladium-loaded catalysts using carbon microsphere supports. By optimising the preparation method, a significant increase in the hydrogenation activity of nitrobenzene and crotonic acid was achieved. Furthermore, it was ensured that the precious metal remains homogeneously distributed on the microspheres surface.

The use of carbon microspheres offers many advantages, including high specific BET surface areas of up to 1,200 m²/g and beneficial properties such as mechanically robust, low pressure drop and easy filtration behaviour.

The platinum and palladium microspheres catalysts show promising results and they can be produced with particle sizes of 200 and 470 µm. By combining these properties, precious metal-based microsphere catalysts have the potential to bridge the gap between batch and continuous production processes in fine chemical and pharmaceutical applications.

Based on this work, new opportunities for catalyst design and application in both batch and continuous systems are emerging. Further research and optimisation of microsphere catalysts will be focused on expanding the portfolio in order to transfer the improvements to other applications and catalyst systems. One such ongoing project is the development of analogous ruthenium-coated microsphere catalysts. ●

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