Catalytic **conversions**

Heraeus Precious Metals has announced a number of advances in catalysts in recent months. **Andrew Warmington** reports

Heraeus Precious Metals, one of the global leaders in the field, used a recent webinar entitled 'Optimising precious metal catalysts for finechem and pharmaceutical applications' to make a number of key announcements. These included a new ligand and a new development process, with a further new catalyst following shortly afterwards.

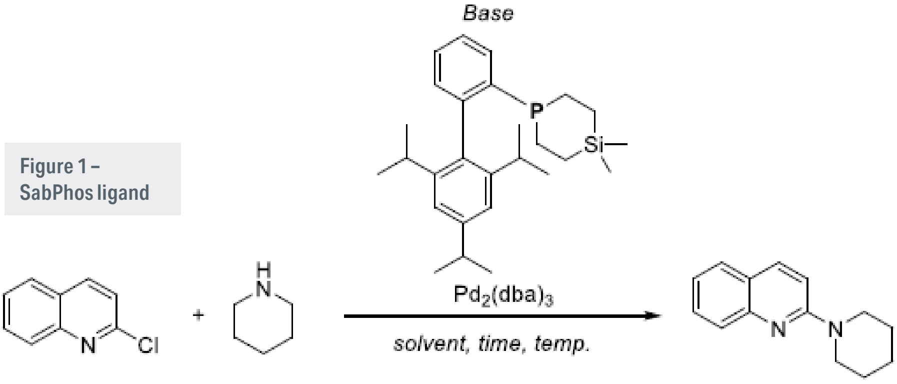

Figure 1 – SabPhos ligand

New ligand

The company developed its new phosphine ligand SabPhos (Figure 1) in partnership with Ludwig Maximilians University in Munich. This is targeted at C-N couplings that were not feasible before. It currently incorporates a palladium-dba complex, but the company is working on using other precious metal supports in it.

"The special feature of SabPhos," said Dr Detlef Gaiser, technical sales manager for homogenous catalysts and precious metal salts, "is that it contains not only a phosphine but also a silicon, which pushes the electrons to the phosphorus and influences the electronic surroundings of the precious metal, in this case a palladium-dba complex."

The conditions of the reaction when using this new catalyst are much milder than with a conventional bulky phospine ligand. It achieves an 88% yield at 60°C in two hours, or 19% at room temperature in three, whereas the traditional ligand takes 24 hours to reach 5%. SabPhos also does not require the use of toluene as solvent.

Heraeus already offers a variety of palladium-phosphine complexes in powder for many different C-C coupling reactions, including the Suzuki, Stille, Sonogashira, Negishi, Hyama and Heck reactions, as well as the Buchwald-Hartwig reaction for direct C-N bond formation in heterocyclic compounds. All are available in kilogram volumes.

The company supplies homogeneous catalysts based on the six different platinum group metals (PGMs) of platinum, palladium, rhodium, ruthenium, iridium and osmium. In addition, it has access to the full variety of inorganic salts that come from these metals, including chlorides, nitrates and ammonium chlorides, which it develops in-house. These are also the starting materials for its heterogeneous catalysts.

New process

Artur Gantarev, technical sales manager for heterogeneous catalysts, said that Heraeus also offers heterogeneous catalysts for similar applications to homogeneous catalysts. These include chemicals, agrochemicals and pharmaceuticals, as well as for gas purification and specialised applications ranging from analytical equipment to satellite propulsion.

Depending on how they are synthesised, these catalysts can be supplied in powder and bulk forms, and in coatings, with the precious metal sitting outside or inside the support material (Figure 2). The choice of precious metal precursor largely controls the behaviour and performance of the catalysts. These materials can also be of many types, such as activated carbon, alumina, silica, alumino-silicate, TiO_2 and zeolites, and their physical characteristics vary considerably.

"Recently we have been getting more and more requests from customers who have been buying powder catalysts from us but want to have the same catalyst for use in a continuous reactor," Gantarev said. However, when the process changes, the customer cannot know at first what the final catalyst will look like and Heraeus has to support it in this journey.

In response, Heraeus has gained exclusive access to a new, specialised support material based on carbon microspheres. With this, it has been able to produce robust and mechanically stable catalysts that can be used in batch and continuous flow processes in tubes, capillaries or micro-structured devices. The catalysts can be used in fast and exothermic reactions and offer good process control and rapid reaction optimisation, said Gantarev.

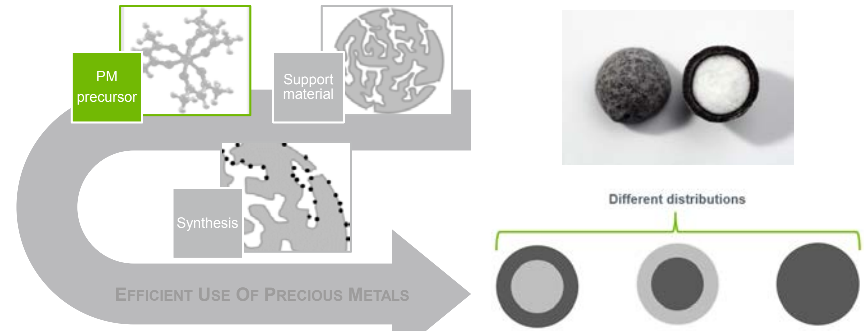

Figure 2 – Catalyst manufacturing at Heraeus

Recycling metals

Recycling is an increasingly important issue when it comes to precious metal catalysts Gaiser noted. Heraeus' recycling and refining processes have yielded about 120 tonnes of PGMs, 370 of gold and 1,270 of silver to date. 60% of the PGMs and 23% of the gold and silver processed in its plants by volume are secondary material.

The company applies a wide range of preparation, sampling and purification techniques to the different materials that come in. By these different means, it can separate out all eight precious metals as well as rhenium and process them into different outputs, including chemical precursors as well as bars, grains and sponges (Figure 3).

Secondary metals like these now account for 24-33% of the process stream and Heraeus aims to push it even higher for both environmental and economic reasons. Not only are the materials intrinsically valuable, when recycled their carbon footprint measured against primary metals in CO_2 eq./gram produced is 97-98% lower for all four PGMs and iridium.

Since 2019, Heraeus has had a goal of being carbon-neutral for its own operations by 2025 and to have completely eliminated fossil fuels and achieved net zero GHG emissions by 2033. Recycling the metals is thus crucial to achieving these targets.

New catalyst

Subsequently, at the P2X conference in Frankfurt in November, Heraeus launched a new ruthenium-based catalyst for proton exchange membrane (PEM) water electrolysis. Developed with South African firm Sibanye-Stillwater, this is said to combine the high activity of ruthenium-based catalysts with unprecedented stability during hydrogen production.

Heraeus said that 40% of the planned 175 GW of hydrogen due onstream by 2030 is expected to be produced using PEM electrolysis, which itself depends on iridium. Today, on average about 400 kg of iridium is required to build one GW of capacity. This needs to be reduced to 100 kg to avoid supply bottlenecks as only 9 tonnes/year of iridium are mined worldwide. The new catalyst can reduce iridium use by 85%.

The new catalyst is said to solve the problem of ruthenium's lack of stability in a PEM electrolyser stack "by combining both ruthenium and iridium oxide in a novel manner, enhancing stability while maintaining the increased catalytic activity provided by ruthenium". It can also achieve up to 50 times higher mass activity compared to iridium oxide, Heraeus said, while accelerated degradation tests confirmed its stability after 30,000 cycles, with significantly lower activity loss than for ruthenium oxide and on a par with iridium oxide. ●

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Figure 3 - Precious metal catalyst recycling at Heraeus