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On the Criticality of Palladium in Organic Synthesis: A Perspective

Palladium-based catalysis: a field with scope for expansion

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The palladium price has been rising because emissions legislation necessitates using more palladium in catalytic converters. However, this trend will not continue as the energy transition progresses, and in the future there will be considerably more palladium available to use in other applications, including chemicals, pharmaceuticals and agrochemicals catalysts. This is both opportunity and justification for the organic chemistry research community to develop new and significant uses for palladium that can be of global benefit. Any catalyst research needs to include optimisation of circular economy, offering sustainable process and recovery options to support life cycle assessment (LCA).

Palladium as a Critical Metal

Palladium is the metal of choice for many catalytic coupling reactions in organic synthesis. It is particularly useful in the homogeneous synthesis of high-value target molecules in the pharmaceutical and agrochemical industries. It features on the UK (1), USA (2) and European Union (EU) (3) critical minerals lists as one of a set of platinum group metals (pgms) which are simultaneously technologically significant, difficult to substitute and sourced in parts of the world where there can be political instability.

Because of its critical metal status, and because metals are by their nature finite resources, some have expressed concern about the future of palladium in organic synthesis (4, 5). For those of us who grew up with a palladium price that was comfortably below those of gold and platinum, the recent price highs (**Figure 1**) stir fears about whether palladium will price itself out of catalyst markets (6).

Why is the palladium price currently so high? Anyone who reads Johnson Matthey's 'PGM Market Report' will be aware that there is currently more demand for palladium than there is palladium to fulfil it (7). This is because palladium is a vital

Fig. 1. Johnson Matthey palladium base price showing variability from 2015 to 2022

metal in catalytic converters, which are required to minimise exhaust emissions. Vehicle emissions limits are subject to increasingly strict legislation in many parts of the world, including China, the USA and Europe. To achieve these stricter emissions limits, the loading of pgm on the catalysts is increasing so more and more palladium is being used by the catalytic converter market.

Palladium in the Chemicals Sector

It may come as a surprise to catalyst chemists to discover that only about 6% of global palladium demand was used in the chemicals sector in the year to April 2022. 83% of the available palladium (**Figure 2**) was used in automotive catalytic converters. This, however, is expected to change as a result of international initiatives to replace the internal combustion engine with battery and fuel cell powered vehicles. In the USA, an executive order for cars and light duty trucks states that "half of all new vehicles sold in 2030 be zero-emissions vehicles" (8), the UK has announced the end of the sale of new non-zero emission cars and vans by 2035, and the European Parliament is backing a European Commission proposal for a total ban on new CO_2-emitting cars and vans by 2035. Declining production of the internal combustion engine will result in declining demand for palladium in its major market. In the later years of the transition, palladium consumption by the chemicals sector has the scope to increase six-fold without constraining supply.

Supply *vs.* Demand

If the demand for palladium in catalytic converters goes down, will market forces not ensure decreased supply of palladium to compensate? Neither historical supply data, nor the economics of palladium refining, indicate that this will occur.

The supply of pgms in a given year comes from three sources: mining, recycling and reserves of above-ground metal (for example, investment bars and jewellery). Over the past 10 years the ratio for palladium of recycled to primary supply has been approaching 1:2 (**Figure 3**). In this period there has been no marked increase in the outputs from mining in response to market demand nor marked decreased due to finite supplies. In fact, mined supply has been relatively flat: while some mines have expanded, and surface stocks have been mobilised in response to strong demand, there has been declining production at other, older mines. Open-loop recycled supply has increased gradually ever since 1984.

Palladium supply is not directly controlled by the market because 90% of palladium mined every year is produced as a byproduct of either platinum or nickel mining. As a result, the availability of palladium is inextricably linked with the supply of the metals it is mined with, and the economics of mining palladium depend on the combined worth of the coextracted metals. In reporting the value of mine output, pgm producers refer to the basket price, which is the combined price of a troy ounce of the particular ratio of pgms, or pgms and gold, that are extracted together. It is the ore, not the market, that determines what that ratio is. The mining sector can influence the longer-term future palladium supply to some degree by selecting whether to develop palladium-rich or palladium-poor deposits but, irrespective of whether palladium is in surplus or deficit, it will continue to be produced as one of a basket of valuable metals.

The same co-dependencies exist in palladium supply from recycling processes. Recycling autocatalysts, which will continue for many years

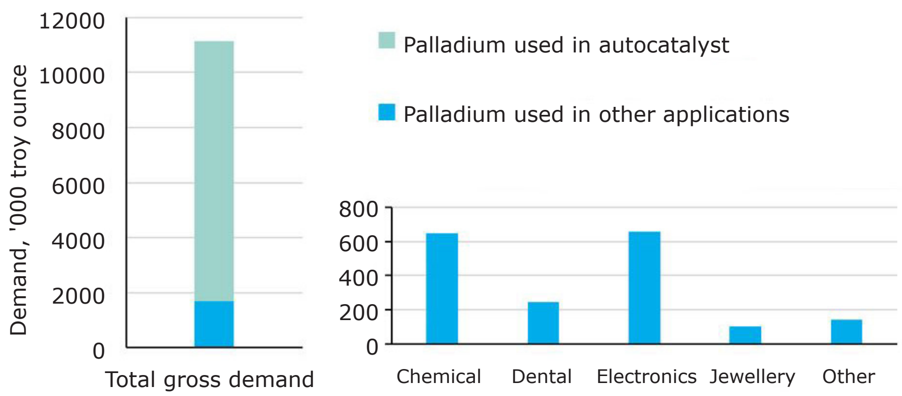

Fig. 2. Proportion of the 2021 demand for palladium taken up by autocatalysts and other applications

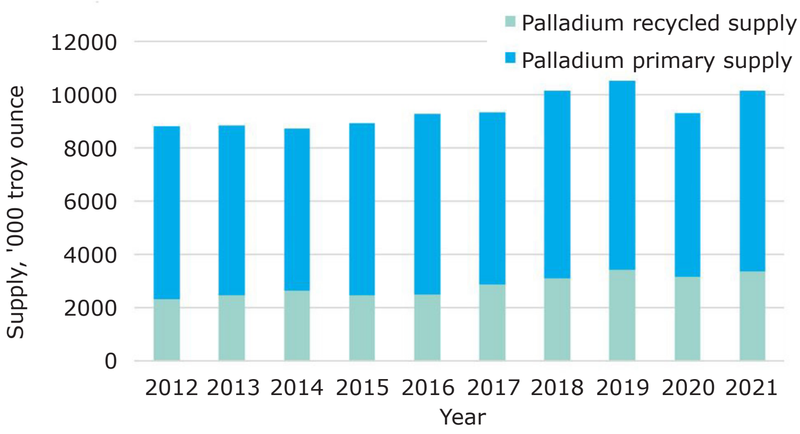

Fig. 3. Amount of palladium produced by mining and by refining over the past 10 years

after the 2030/2035 turning point, necessitates refining palladium along with rhodium and platinum. Even in jewellery platinum can be alloyed with some palladium. As long as alloys and mixtures of pgms are recycled, palladium will continue to be produced.

Palladium for the Future

The fact that in the longer term there will be plenty of palladium for use in manufacturing is good news for the synthetic organic chemist, and for global dependence on agriculture and the pharmaceutical industry. But if the availability of palladium results in its price decreasing long term, what impact is that likely to have on the other pgms which are palladium's coproducts?

Technologies for the energy transition need metals with good electrochemical and catalytic properties, that withstand extreme conditions and do not corrode. The pgms are unique in their ability to do this. Examples include platinum in fuel cells, iridium in proton exchange membrane electrolysers and all the pgms in process catalysts for sustainable and bio-derived fuels (9). But if the price of palladium goes down because future availability exceeds market demand, it will become economically less favourable to mine and recycle all of the pgms. This will have little impact on the availability of palladium to the chemicals sector but could limit supply of other pgms into alternative energy technologies, which the world urgently needs.

The solution to this problem is that we are going to need to use more palladium in the future. Only by using more palladium will it be possible to justify continuing to mine and recycle all the pgms. Having more applications of palladium will put supply of all the pgms on a more sustainable footing by making mining and processing more economically viable, but also by ensuring that the valuable byproducts are not wasted. And as long as that palladium becomes part of the circular economy, it will contribute to long-term future availability.

From the perspective of pgms being a scarce and finite resource, this solution may appear counterintuitive. However, the thesis of this paper is that finding new applications for palladium is a necessary step in protecting the future availability of all the pgms. This conclusion is justification and opportunity for the scientific community, and particularly for the fine chemicals industry, to focus efforts on inventing the new, high-volume applications of palladium that will be required. And given it can take 10 years to go from laboratory to plant, the time to start inventing those applications is now.

Recognising this, the pgm industry is actively searching for new applications for palladium. The Global Palladium Fund was established in 2016 with the remit "to advance the development of world-changing technologies in essential areas such as aerospace, electronics, and the automotive industries" and in 2022, with sponsorship from Nornickel, the International Precious Metals Institute issued the Palladium Challenge (on hold at the time of writing due to subsequent developments) to expand the scope of applications that use palladium. Johnson Matthey, too, is giving away samples of palladium and other pgms to encourage research into new applications (10).

Palladium Sustainability

Achieving net-zero goals is a challenge that has been taken to heart by the chemistry community. Where previously cost and catalyst performance were the deciding indicators of success, the past decade reveals an increasing focus on the conditions and environmental impact of catalyst-mediated processes (5). Reaction conditions that have the potential to contribute to a sustainable process include: using less palladium (thrifting); avoiding organic solvents in favour of water (11); processing at ambient temperature; one-pot reactions; using recycled palladium; recovering ligands; using stoichiometric reagent instead of excess. Which of these parameters actually contribute to a sustainable process is a complex question.

Take thrifting. Metal is generally thrifted to decrease manufacturing costs and minimise the value locked up in a batch of catalyst. Ground-breaking research has proved that it is possible to decrease palladium catalyst loadings significantly while maintaining and, in some cases, improving catalyst performance (12). Thrifting is unquestionably a good way to ensure scarce metals are more widely available. The drawback is that thrifting can make recycling more difficult. The less pgm there is in a catalyst, or the more performance additives it contains, the more difficult the metal can be to recover at the end of life and the more waste can be produced. In a market-driven industry, if the cost of recycling exceeds the value of the pgm, there is no economic motivation to recover the metal.

A significant step towards solving this would be to include circular economy as an intrinsic parameter of catalyst performance, alongside yield, selectivity, cost and turnover number. In this paradigm, a good catalyst is one from which the palladium (or any critical metal) can easily be recovered at end of life. And it's not just about reusing the metal. Currently, in recovering the palladium from some homogeneous catalysts, the sophisticated and expensive ligands required to tune the catalytic reaction are burned. Being able to recover undegraded ligands as well as metal from the end-of-life mixture has the potential to decrease both the cost and environmental impact of a process. This is an avenue of investigation that the research community is ideally placed to follow: those who put the catalyst together are surely best placed to understand how it can be taken apart again most efficiently at end of life. Doing the recycling research alongside new catalyst development builds design for recycle into the catalyst discovery process and creates a product tailored for the net zero future.

Does using recycled palladium contribute to a sustainable process? With today's technology, recycled pgms have much less environmental impact than newly mined pgms, so using recycled palladium improves the sustainability metrics of the individual process. The global picture is more complicated. The world currently uses all of the palladium available, whether mined or recycled. If the size of the market were unchanging, one process using recycled metal would just mean another process has to use mined metal and there would be no global impact of using one over the other. However, at the moment the demand for palladium is greater than what is produced. If that demand can be met by producing more recycled metal rather than mining more metal, then there is a global sustainability benefit to using recycled palladium in a catalyst.

Throughout this section, care has been taken to use 'potential' in phrases such as 'decrease in environmental impact'. Actually it's impossible to know whether adopting 'sustainable' reaction conditions will result in a lower environmental impact across the whole life cycle of the catalyst. The only way to be sure is to do the LCA. However, it is essential to do research to develop more eco-friendly process options that avoid ecotoxic solvents, excesses of reagents or high energy use because it gives the process chemist the best range of alternatives when it comes to comparing process options in the LCA.

Conclusion

Palladium will become increasingly available in the longer term as the energy transition proceeds towards and beyond the 2030/2035 turning point. Rather than constraining research or substituting less satisfactory alternative metals because the palladium price is currently high, this is the time when synthetic organic chemists need to be developing the future palladium catalysts on which the chemical, pharmaceutical and agrochemical sectors depend.

New catalysts will need to become part of a circular economy where recovery and reuse of the palladium and its ligands are an intrinsic feature of catalyst design. And using tools such as LCA to evaluate routinely which process options have minimum environmental impact will ensure chemical processes are ever more sustainable.

Beyond this opportunity in palladium catalysis, there is a need for broader use of palladium in the future. The circular economy of the pgms depends on all of the metals that are co-mined or co-recycled contributing to the economic viability of processing. Making beneficial use of more palladium in future safeguards the availability of the other pgms which are critical to the net zero transition.

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