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Challenges in (homogeneous) catalysis with precious metal catalysts

5 November 2024

Antonio Zanotti, Jane Patrick, Sarah Facchetti

About Platinum Group Metals

The platinum group metals (PGMs)

Periodic Table of the Elements

Atomic Number → 1 ← Symbol
 Name → ← Atomic Weight

1 1A H Hydrogen 1.008																	18 VIII A He Helium 4.002602																														
3 Li Lithium 6.94	4 2A Be Beryllium 9.0121831											5 3A B Boron 10.81	6 4A C Carbon 12.011	7 5A N Nitrogen 14.007	8 6A O Oxygen 15.999	9 7A F Fluorine 18.998403163	10 8A Ne Neon 20.1797																														
11 Na Sodium 22.98976928	12 2A Mg Magnesium 24.305											13 3A Al Aluminium 26.9815385	14 4A Si Silicon 28.085	15 5A P Phosphorus 30.973761998	16 6A S Sulfur 32.06	17 7A Cl Chlorine 35.45	18 8A Ar Argon 39.948																														
19 K Potassium 39.0983	20 2A Ca Calcium 40.078	21 3 Sc Scandium 44.955908	22 4 Ti Titanium 47.867	23 5 V Vanadium 50.9415	24 6 Cr Chromium 51.9961	25 7 Mn Manganese 54.938044	26 8 Fe Iron 55.845	27 9 Co Cobalt 58.933194	28 10 Ni Nickel 58.6934	29 11 Cu Copper 63.546	30 12 Zn Zinc 65.38	31 13 Ga Gallium 69.723	32 14 Ge Germanium 72.630	33 15 As Arsenic 74.921595	34 16 Se Selenium 78.971	35 17 Br Bromine 79.904	36 18 Kr Krypton 83.798																														
37 Rb Rubidium 85.4678	38 2A Sr Strontium 87.62	39 3 Y Yttrium 88.90584	40 4 Zr Zirconium 91.224	41 5 Nb Niobium 92.90637	42 6 Mo Molybdenum 95.95	43 7 Tc Technetium (98)	44 8 Ru Ruthenium 101.07	45 9 Rh Rhodium 102.90550	46 10 Pd Palladium 106.42	47 11 Ag Silver 107.8682	48 12 Cd Cadmium 112.414	49 13 In Indium 114.818	50 14 Sn Tin 118.710	51 15 Sb Antimony 121.760	52 16 Te Tellurium 127.60	53 17 I Iodine 126.90447	54 18 Xe Xenon 131.293																														
55 Cs Caesium 132.90545196	56 2A Ba Barium 137.327	57 - 71 Lanthanoids	72 6 Hf Hafnium 178.49	73 7 Ta Tantalum 180.94788	74 8 W Tungsten 183.84	75 9 Re Rhenium 186.207	76 10 Os Osmium 190.23	77 11 Ir Iridium 192.222	78 12 Pt Platinum 195.084	79 13 Au Gold 196.966569	80 14 Hg Mercury 200.592	81 15 Tl Thallium 204.38	82 16 Pb Lead 207.2	83 17 Bi Bismuth 208.98040	84 18 Po Polonium (209)	85 19 At Astatine (210)	86 20 Rn Radon (222)																														
87 Fr Francium (223)	88 2A Ra Radium (226)	89 - 103 Actinoids	104 6 Rf Rutherfordium (261)	105 7 Db Dubnium (268)	106 8 Sg Seaborgium (269)	107 9 Bh Bohrium (270)	108 10 Hs Hassium (278)	109 11 Mt Meitnerium (276)	110 12 Ds Darmstadtium (281)	111 13 Rg Roentgenium (282)	112 14 Cn Copernicium (285)	113 15 Nh Nihonium (286)	114 16 Fl Flerovium (289)	115 17 Mc Moscovium (289)	116 18 Lv Livermorium (293)	117 19 Ts Tennessine (294)	118 20 Og Oganesson (294)																														
<table border="1"> <tr> <td>57 La Lanthanum 138.90547</td> <td>58 Ce Cerium 140.116</td> <td>59 Pr Praseodymium 140.90766</td> <td>60 Nd Neodymium 144.242</td> <td>61 Pm Promethium (145)</td> <td>62 Sm Samarium 150.36</td> <td>63 Eu Europium 151.964</td> <td>64 Gd Gadolinium 157.25</td> <td>65 Tb Terbium 158.92535</td> <td>66 Dy Dysprosium 162.500</td> <td>67 Ho Holmium 164.93033</td> <td>68 Er Erbium 167.259</td> <td>69 Tm Thulium 168.93422</td> <td>70 Yb Ytterbium 173.045</td> <td>71 Lu Lutetium 174.9668</td> </tr> <tr> <td>89 Ac Actinium (227)</td> <td>90 Th Thorium 232.0377</td> <td>91 Pa Protactinium 231.03588</td> <td>92 U Uranium 238.02891</td> <td>93 Np Neptunium (237)</td> <td>94 Pu Plutonium (244)</td> <td>95 Am Americium (243)</td> <td>96 Cm Curium (247)</td> <td>97 Bk Berkelium (247)</td> <td>98 Cf Californium (251)</td> <td>99 Es Einsteinium (252)</td> <td>100 Fm Fermium (257)</td> <td>101 Md Mendelevium (258)</td> <td>102 No Nobelium (259)</td> <td>103 Lr Lawrencium (260)</td> </tr> </table>																		57 La Lanthanum 138.90547	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90766	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93033	68 Er Erbium 167.259	69 Tm Thulium 168.93422	70 Yb Ytterbium 173.045	71 Lu Lutetium 174.9668	89 Ac Actinium (227)	90 Th Thorium 232.0377	91 Pa Protactinium 231.03588	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (260)
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44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42
76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.084

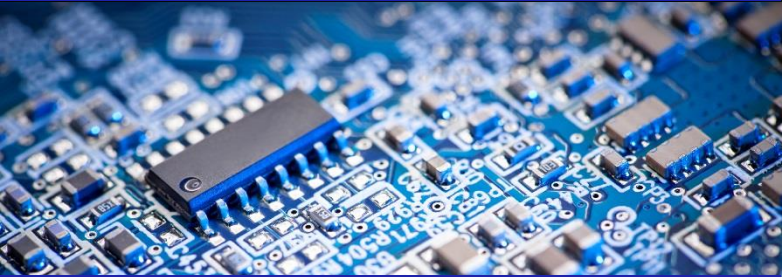
- Platinum
- Palladium
- Rhodium
- Ruthenium
- Iridium
- Osmium



Global markets for PGMs



Automotive



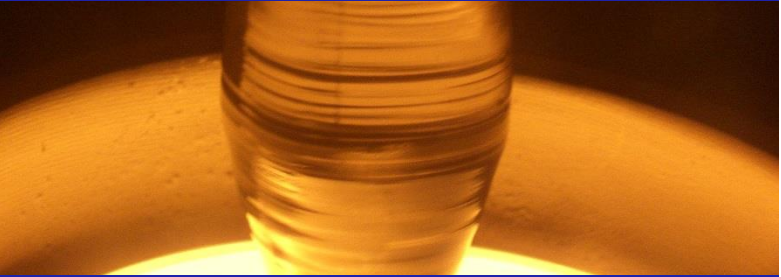
Electronics/Sensors



Pharma



Aerospace



Crystal growth



Agro



Glass



Jewellery





Chemical


Introducing Johnson Matthey in the PGM landscape

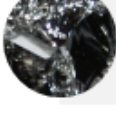
PGMs are high demand precious metals ...

 Palladium

 Platinum


 Rhodium


 Iridium


 Ruthenium



... critical enablers for current and emerging applications

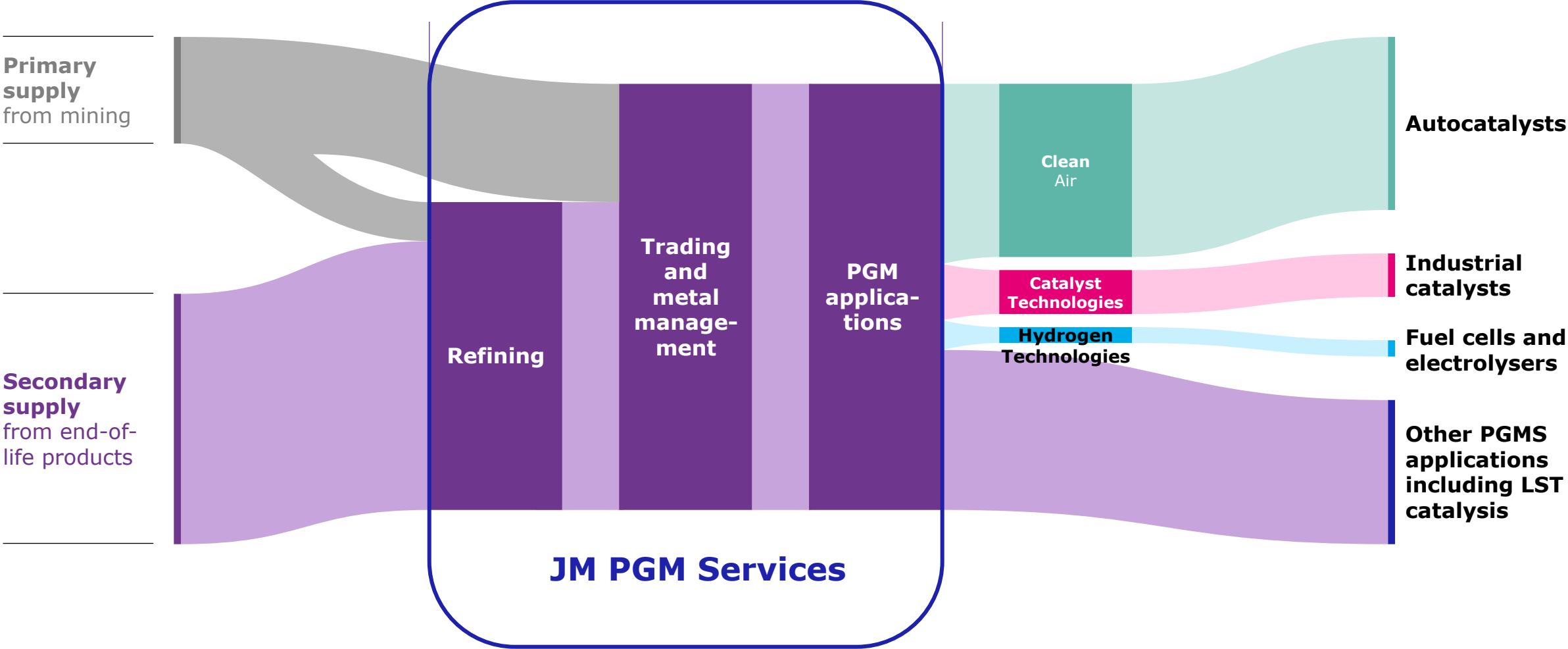
Autocatalysts 

Industrial applications 

Fuel cells 

Life Sciences Technologies 

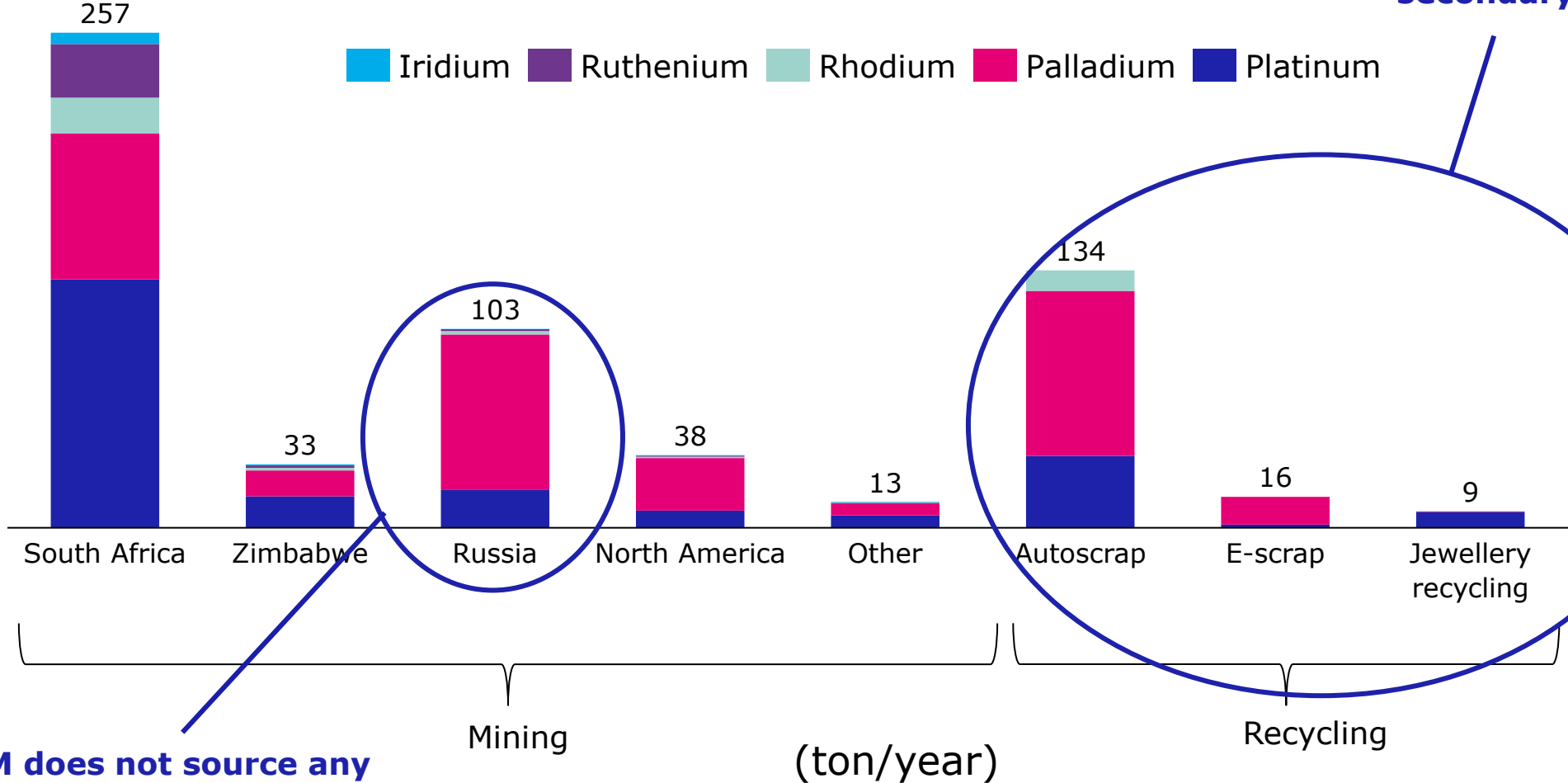
Introducing Johnson Matthey in the PGM landscape



Snapshot of PGM supply

Sources of PGM supply in 2023 (excluding closed-loop recycling)

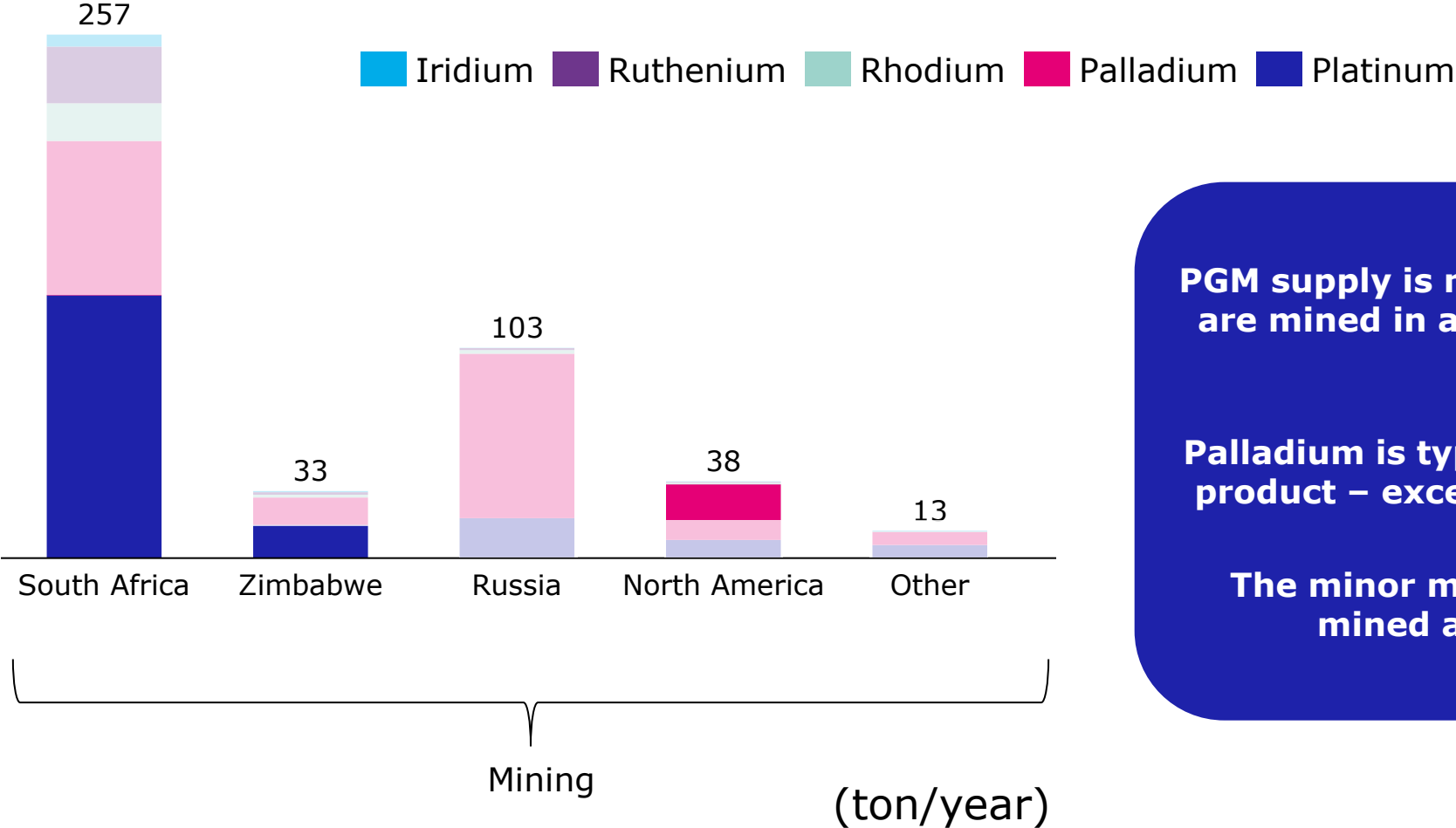
~ 70% PGM used in JM products is from secondary supply



JM does not source any metal from Russia

Snapshot of PGM supply

Sources of mined PGM supply in 2023

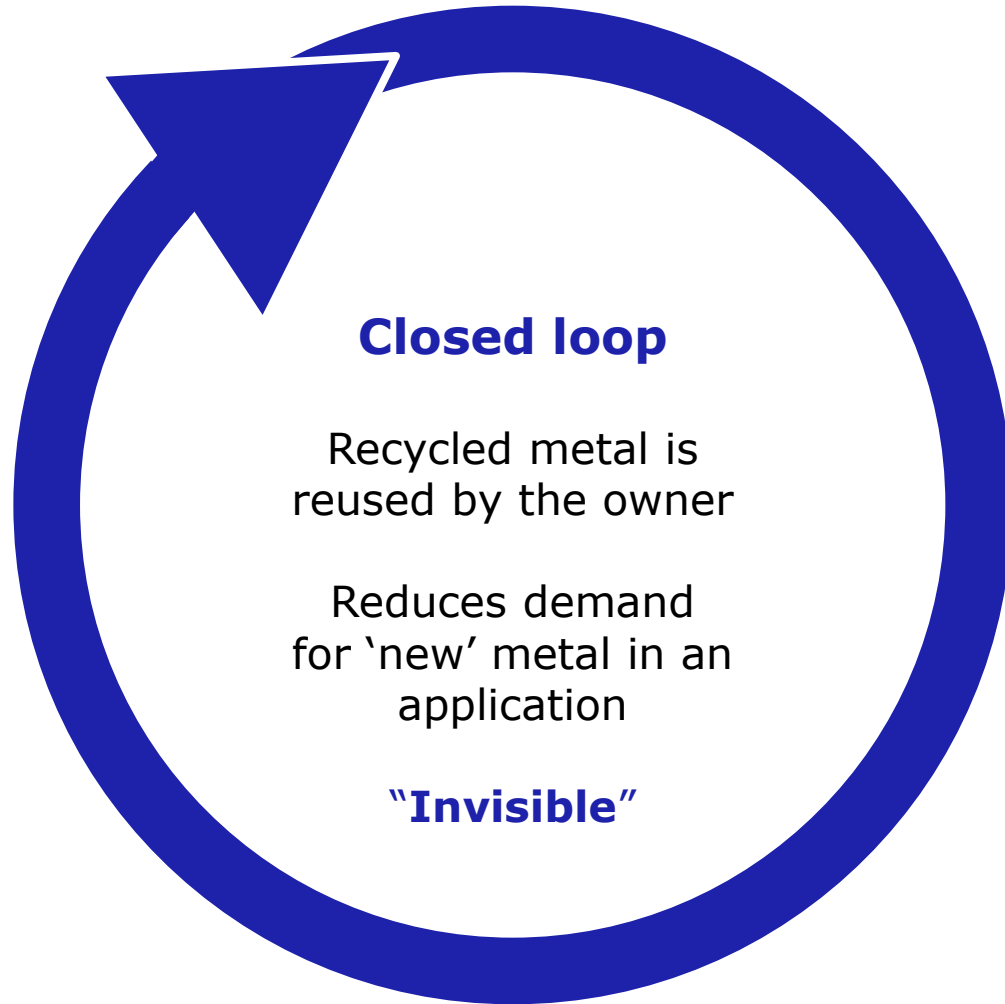


PGM supply is not elastic: the metals are mined in association with each other

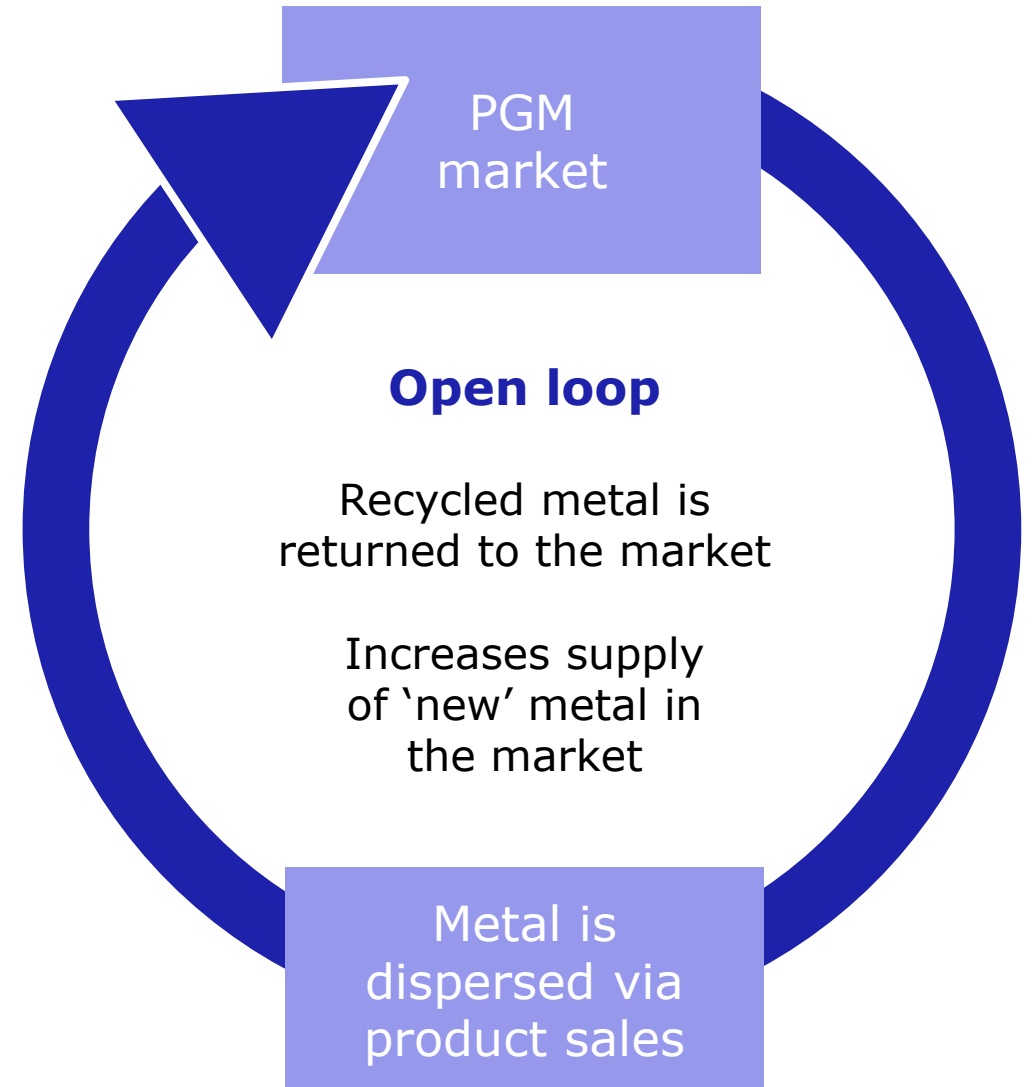
Palladium is typically mined as a co-product – except in North America.

The minor metals are only ever mined as by-products

The different recycling loops



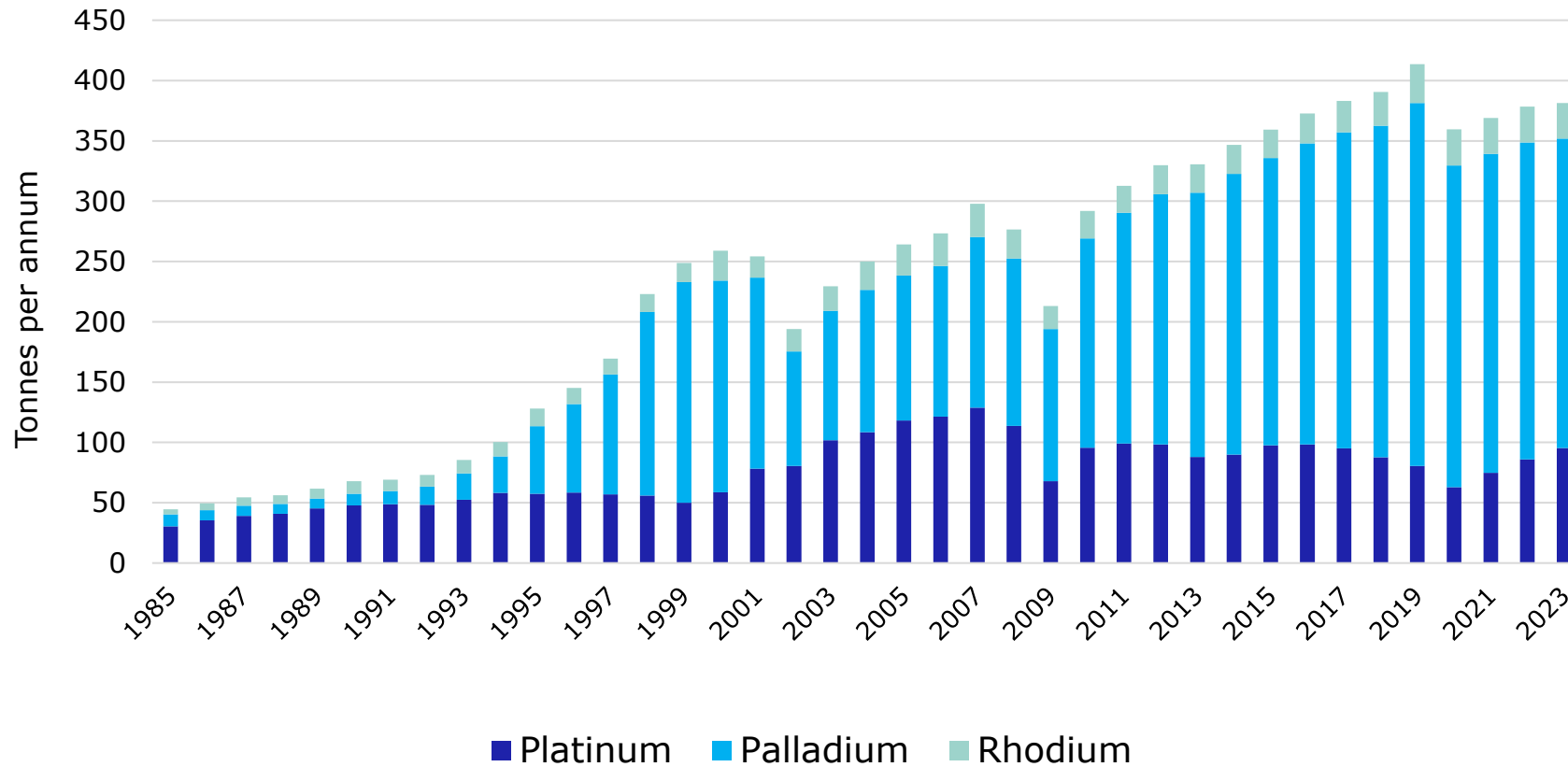
+



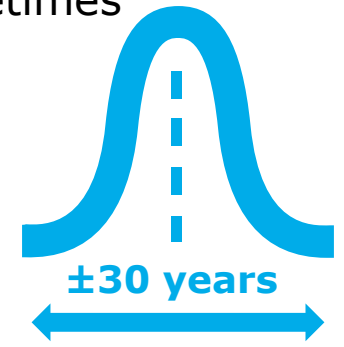
The urban mine

A source of low-carbon metal that can continue for decades

PGM used on new catalytic converters since 1985

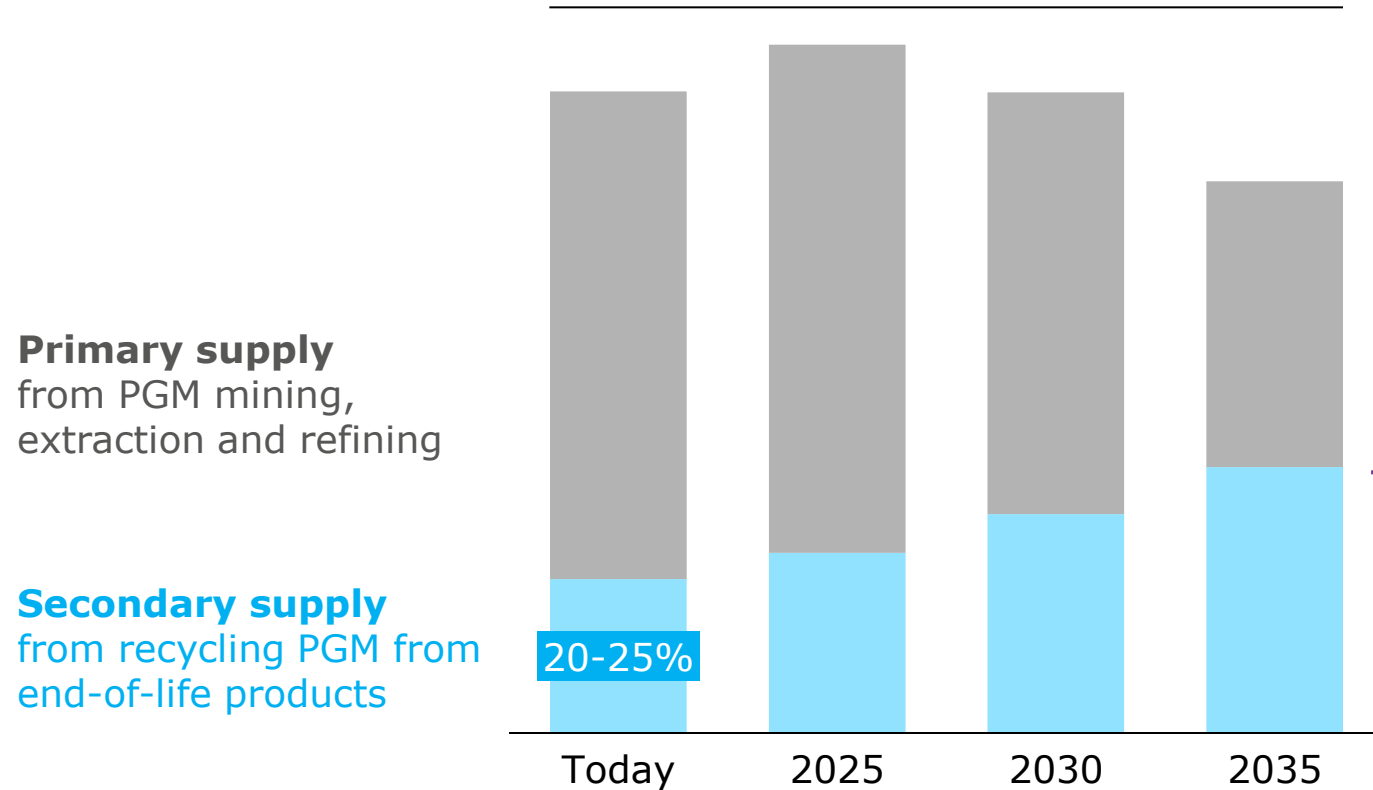


Available for recovery at end of vehicle lifetimes



Recycled metals: critical raw materials management

Market supply of PGM volumes excluding closed loop supply



Primary supply
from PGM mining,
extraction and refining

Secondary supply
from recycling PGM from
end-of-life products

20-25%

The world will continue to require PGMs

Decarbonisation trends make the recycling model even more relevant in the future due to:

- Cost advantage
- Lower carbon content
- Circularity
- Supply security

Lots of information on our website

<https://matthey.com/pgm-markets>



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A guide to PGMs

Understanding the fundamentals of platinum group metals



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Platinum Group Metal Supply Chains: Mature and Global



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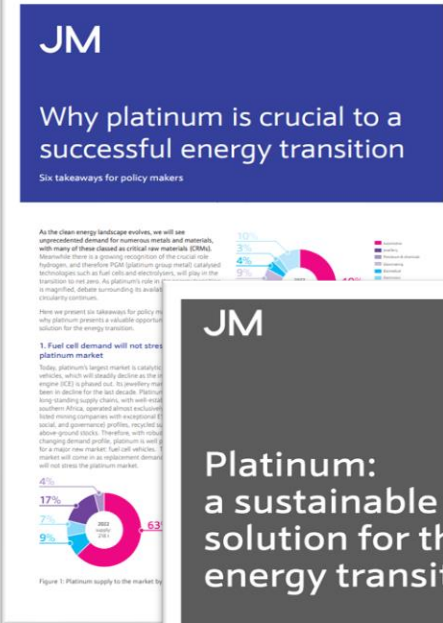


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Why critical metals efficiency is essential for the clean energy transition



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Why platinum is crucial to a successful energy transition

Six takeaways for policy makers

As the clean energy landscape evolves, we will see unprecedented demand for numerous metals and materials, with many of these listed as critical raw materials (CRMs). Meanwhile there is a growing recognition of the crucial role hydrogen, and therefore PGM (platinum group metal) catalyzed technologies such as fuel cells and electrolyzers, will play in the transition to net zero. As platinum's role in this transition is magnified, debate surrounding its availability continues.

Here we present six takeaways for policy makers on why platinum presents a valuable opportunity for the energy transition.

1. Fuel cell demand will not stress platinum market

Today, platinum's largest market is catalytic converters, which will steadily decline as the internal combustion engine (ICE) is phased out. Its jewelry market has been in decline for the last decade. Platinum long-standing supply chains, with well-established mining companies with exceptional ESG social and government profiles, recycled and above-ground stocks. Therefore, with rising changing demand profiles, platinum is well positioned for a major new market. Fuel cell vehicles, 1 market will come as replacement demand will not stress the platinum market.




Figure 1: Platinum supply to the market by region

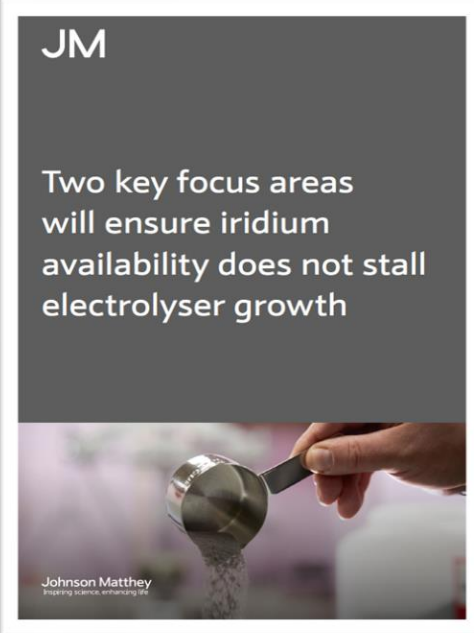


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Platinum: a sustainable solution for the energy transition




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Two key focus areas will ensure iridium availability does not stall electrolyser growth



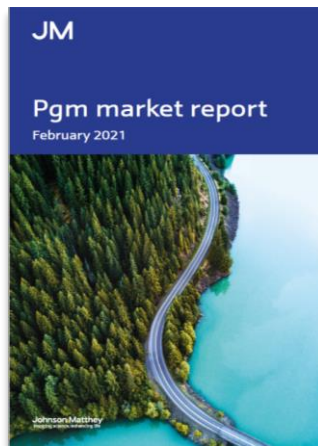
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PGMS Market Research

- Team of analysts dedicated to analysis of the platinum group metals markets
- Principal authority on the pgm markets globally
- Deep insight into end-use product applications and markets, primary supply and recycling
- Short and long-term analysis for internal and customer strategic planning

Public domain resources

PGM Market Report



The PGM supply/demand equilibrium

<https://www.youtube.com/watch?v=n7BjuMqTADg>

PGM refining

<https://www.youtube.com/watch?v=Vn4wnz5KSAM>

Fundamentals of PGMs

<https://www.youtube.com/watch?v=QV0Ehx-MjJg>

Platinum group metals: a circular solution for a net zero future

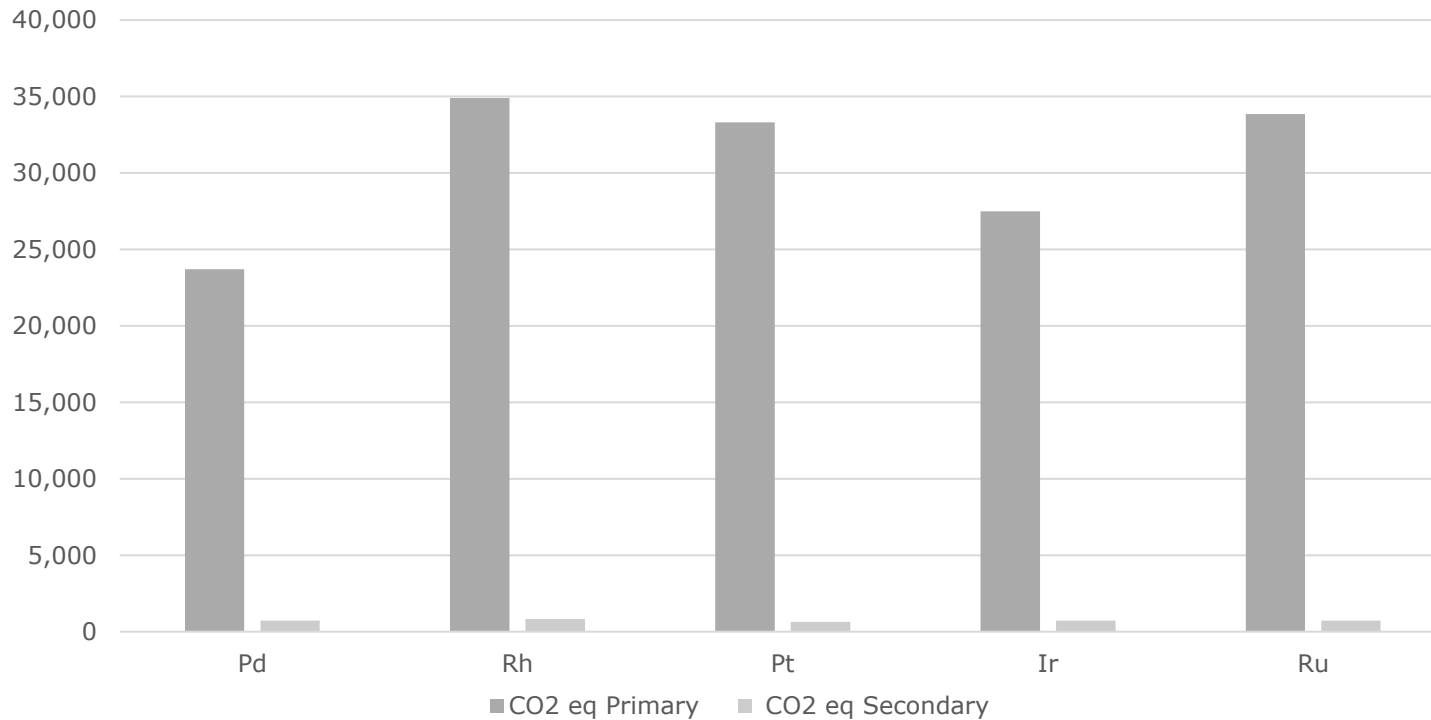
<https://youtu.be/TeCvxN2Qo4U?si=htjGBZB-32PaEmrp>



About a catalyst's footprint in a catalytic step

The carbon footprint of PGMs

CO₂ eq of primary and secondary PGMs



Recycled PGMs have a global warming contribution (CO₂ eq) 30/50 times lower than mined PGMs

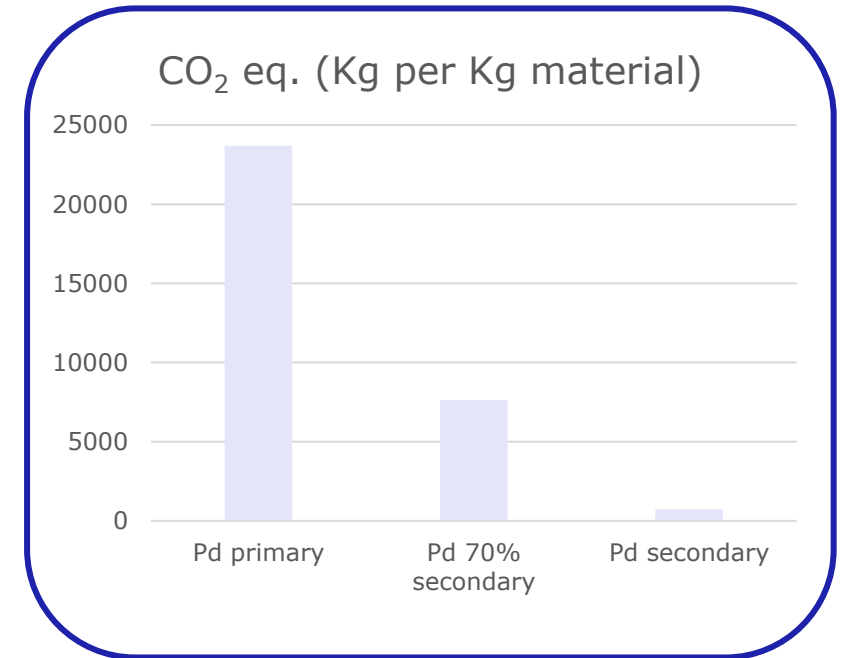
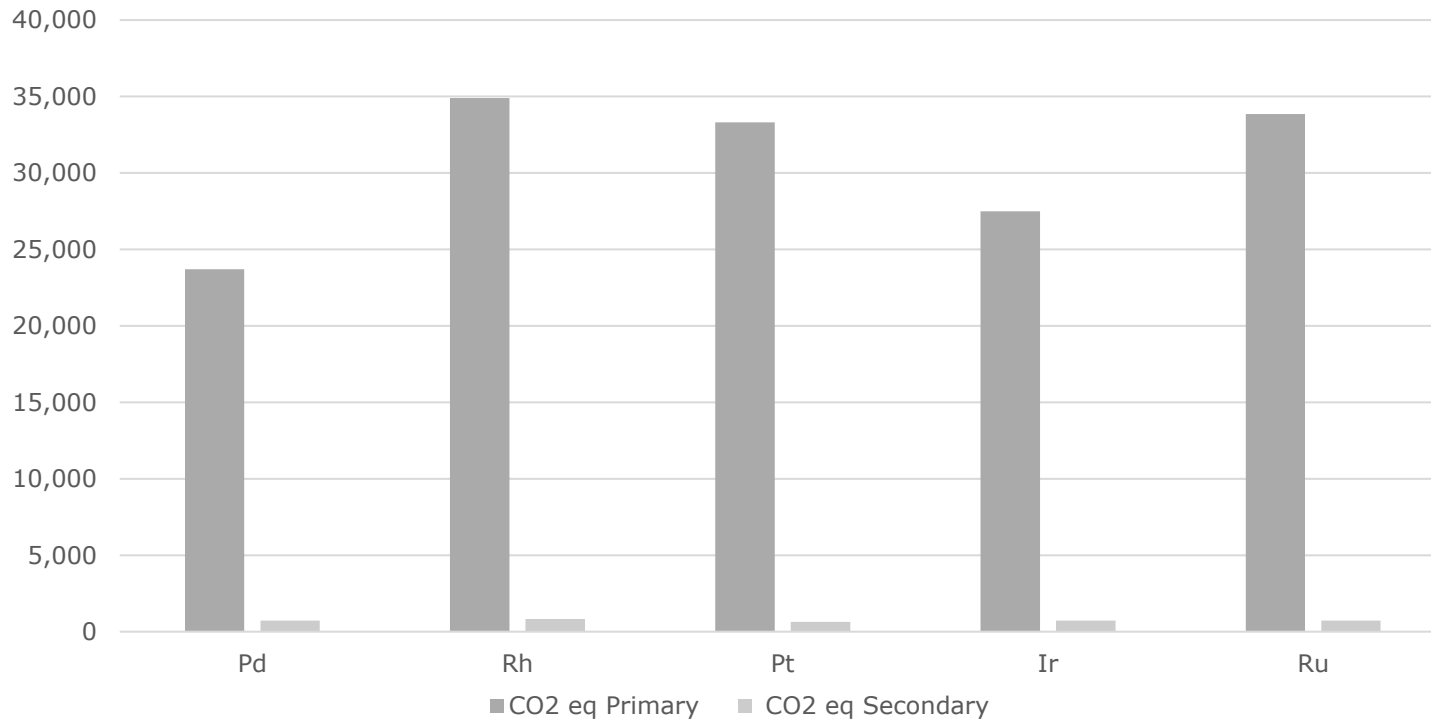
	CO ₂ eq Primary	CO ₂ eq Secondary
Pd	23,700	732
Rh	34,900	819
Pt	33,300	639
Ir	27,500	730
Ru	33,864	730

Source: 'Life Cycle Assessment of Global Platinum Group Metals Production' created by Sphera on behalf of The International Platinum Group Metals Association (IPA), v1.9, 20/10/2020 - Shannon Boonzaier, Christoph Hoppe, Johannes Gediga.

<https://www.ipa-news.com/index/sustainability/lca-data-access.html>

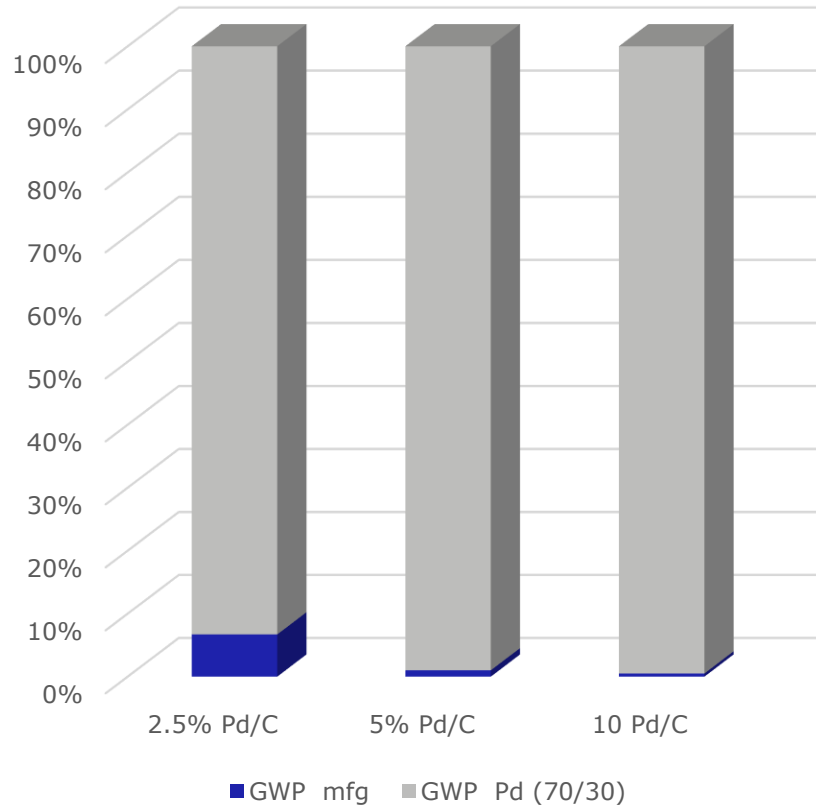
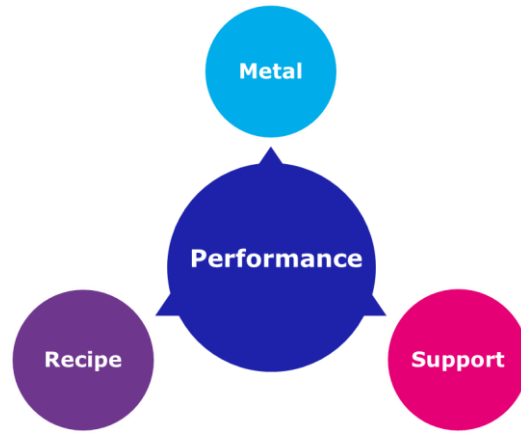
The carbon footprint of PGMs

CO₂ eq of primary and secondary PGMs



Certified 100% secondary metal is available

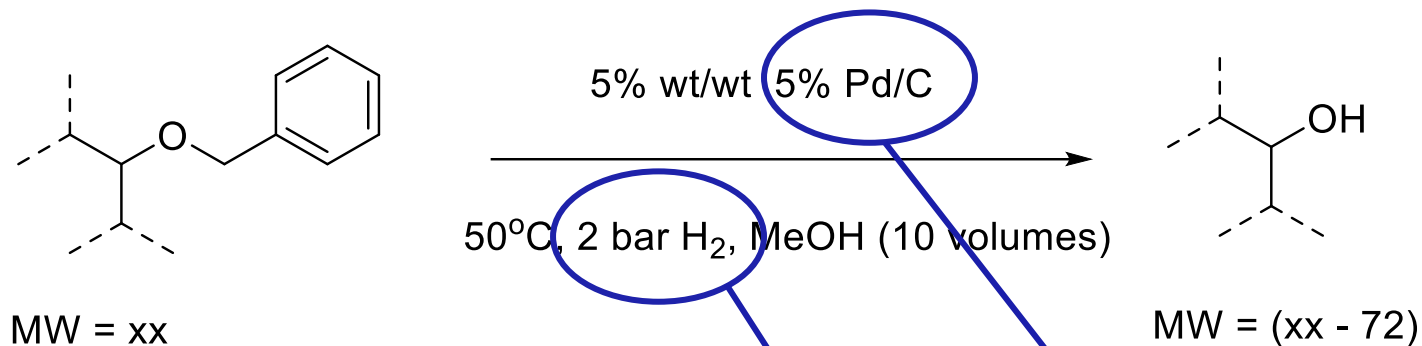
Heterogeneous catalysts



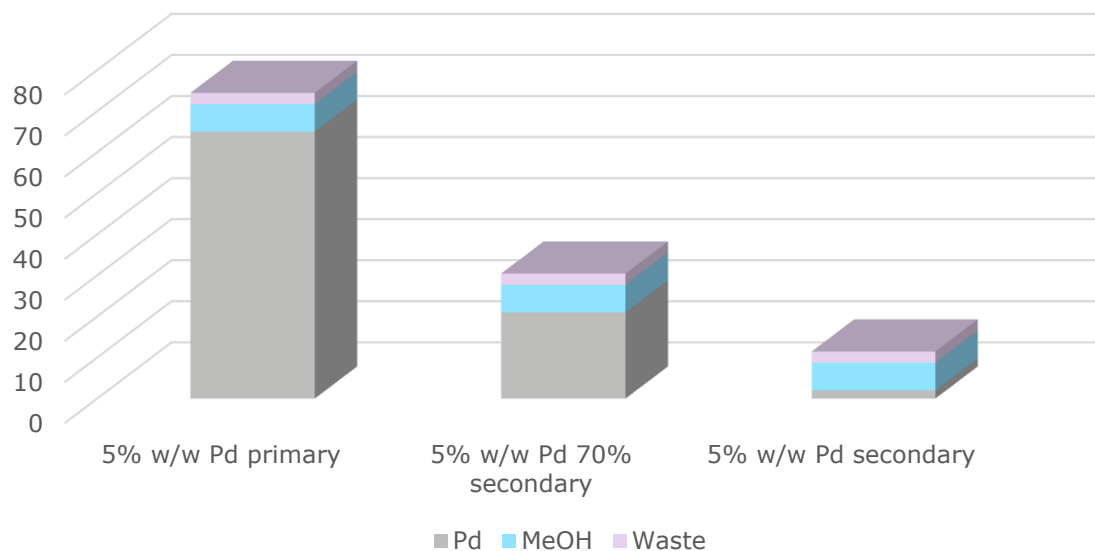
Manufacturing footprint of Pd/C is mostly negligible vs metal footprint

	Pd(Pb)/CaCO3	Pd, Pt(Bi)/C	Pd/Al2O3	Pd/BaSO4	Pd/C	Pd/CaCO3	Pt(Bi)/C	Pt(S)/C	Pt/C	Pt/Graphite	Rh/Al2O3	Rh/C	Ru/Al2O3	Ru/C
Alcohol Oxidation		Light Blue					Red		Red					Dark Purple
Carbocycles					Light Blue			Red			Light Green	Light Green	Dark Purple	Dark Purple
Heterocycles					Light Blue			Red				Light Green		
Alkyne & Alkenes to Alkanes			Light Blue	Light Blue	Light Blue	Light Blue		Red				Light Green		
Alkyne to Alkenes	Light Blue					Light Blue								
Alkyl Aldehydes & Ketones								Red						Dark Purple
Aromatic Aldehydes & Ketones					Light Blue							Light Green		Dark Purple
Unsaturated Aldehydes & Ketones								Red	Red					
Dehydrogenation					Light Blue									
Hydrodehalogenations				Light Blue	Light Blue									
Nitrogen Deprotection					Light Blue									
Oxygen Deprotection					Light Blue									
Ring Opening					Light Blue									
Imines & Oximes					Light Blue				Red			Light Green		
Nitriles					Light Blue				Red			Light Green		
Nitro, Nitroso & Halonitroaromatic					Light Blue			Red	Red					
Red Aminations & Alkylations					Light Blue			Red	Red					
Transfer Hydrogenation					Light Blue									

The carbon footprint of a Pd/C hydrogenation step



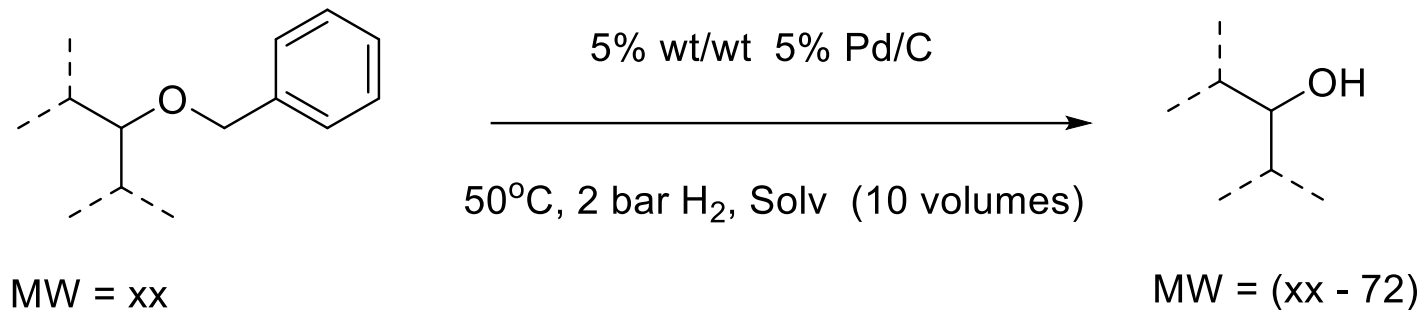
Impact of Pd origin on CO₂ eq contribution to the reaction



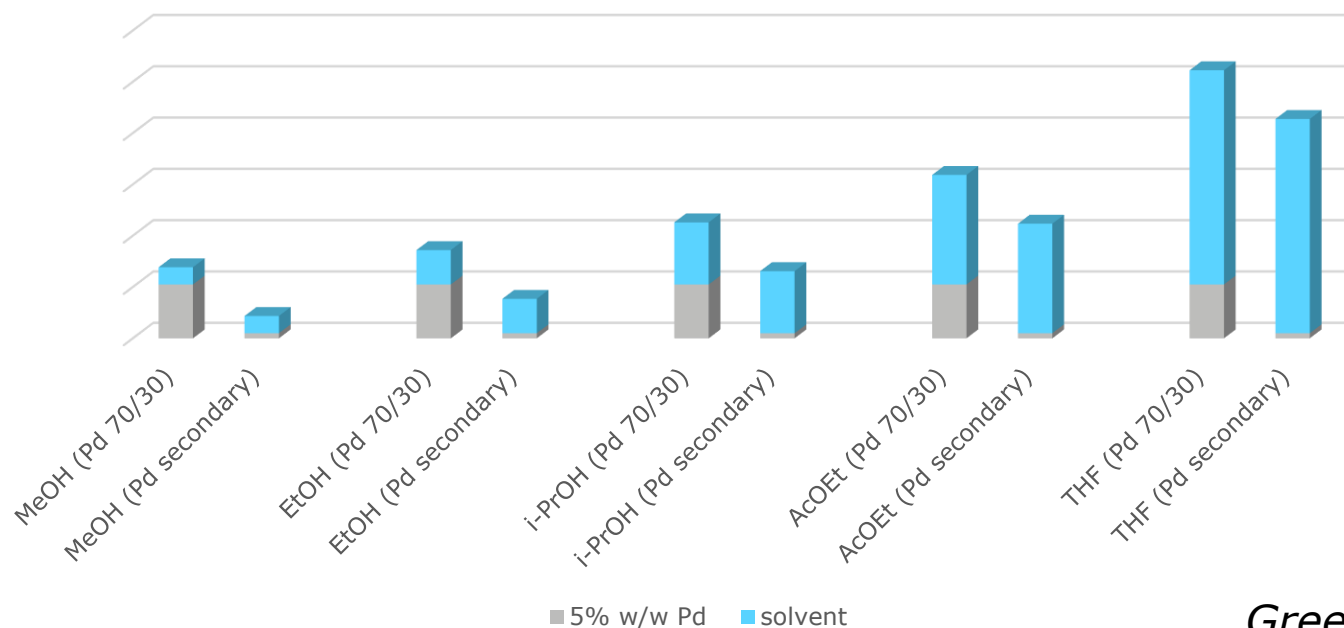
Manufacturing footprint negligible vs metal footprint

Hydrogen contribution negligible: 2g of H₂ per Kg of product

The carbon footprint of Pd/C hydrogenation step



Impact of solvents on GWP of catalytic step



The choice of solvent has a major impact on the catalyst step GWP

Note that selection purely based on GWP (CO₂ eq.) of solvents may differ from selection based on combined other metrics, e.g.:

Green Chem **2016**, 18, 3879 (GSK)

Green Chem **2016**, 18, 288 (GSK, Sanofi, Pfizer)

About base metal catalysts vs PGM catalysts

Growing interest for base metal catalysts

Recent advances in nonprecious metal catalysis

Ickes *et al. Org.Process.Res.Dev* **2023**, 27, 423

Collaboration as a key to advance capabilities for earth abundant metal catalysis

Wisniewski *et al. Org.Process.Res.Dev* **2023**, 27, 1160

Diversification of pharmaceutical manufacturing processes: taking the plunge into the non-PGM catalyst pool

Engle, Seechurn *et al. ACS Catal.* **2024**, 9708

Advances in Earth abundant metal catalysis

Wheelhouse *et al. Org. Process Res. Dev.* **2023**, 27, 1157

For a different point of view see:

B. Lipshutz *Johnson Matthey Technol. Rev.* **2023**, 67, 278

E. Schofield *Johnson Matthey Technol. Rev.* **2023**, 67, 285

Sustainability of Ni and Pd coupling processes

	CO ₂ eq catalyst preparation	CO ₂ eq catalyst contribution in process	CO ₂ eq entire process
Ni	17.5	0.19	2326
Pd	11,289	2.37	1554

Ni catalysis is not necessarily more sustainable than Pd catalysis, but it should be regarded as complementary

Look at the big picture!

From: M. U. Luescher, F. Gallou and B. H. Lipshutz, *Chem. Sci.*, **2024**, DOI: 10.1039/D4SC00482E

Interactions of multiple metrics and environmental indicators to assess processes, detect environmental hotspots and guide future development
M.U. Luescher, F. Gallou *Green. Chem.* **2024**, 26, 5239

Sustainability of Ni and Pd coupling processes

More about cost:

An example of route comparisons in C-H activation:

Ni > **Pd** > **no cat** > **Rh** > **Co** > **Ru**

A.K. Komarova, D.S. Perekalin
Organometallics **2023**, 42, 1433

More about toxicity:

Toxicity of metal compounds:
knowledge and myths

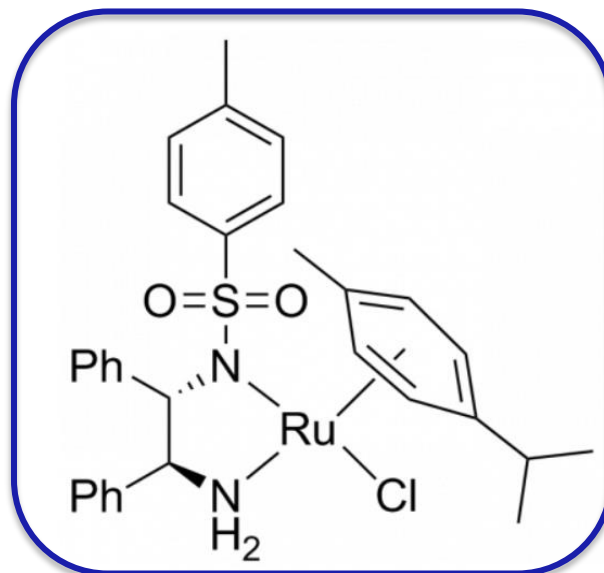
K.S. Egorova, V.P. Ananikov
Organometallics **2017**, 36, 4071

About the importance of process optimization

Asymmetric transfer hydrogenation

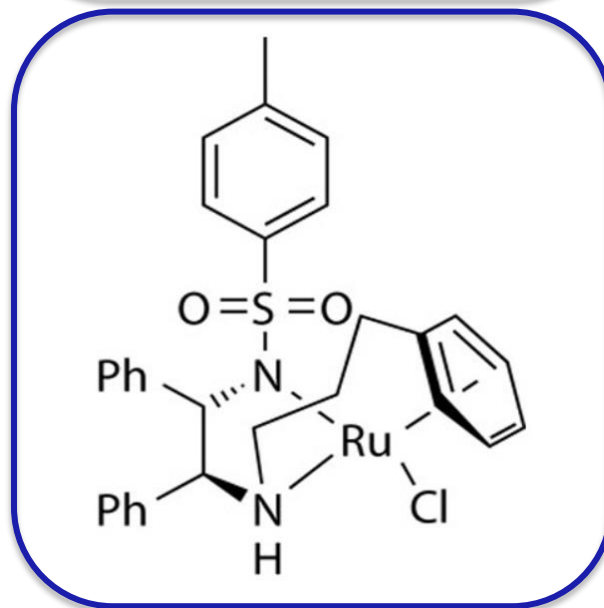
First Generation (Noyori)

- Reliable and flexible
- Well-understood scope
- Cost-effective



Second Generation (Wills)

- Special applications
- Enable the 'impossible'



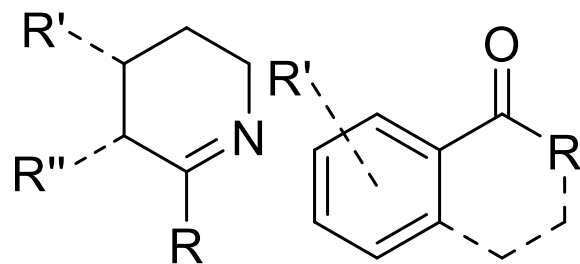
'New transfer hydrogenation patents granted at a stable rate of around 50 per year'

Glorius, Leker *et al.*
Adv.Synth.Catal **2020**, 362, 1258

Catalyst loading in transfer hydrogenation

The 'simple' substrates

	Molar catalyst loading	Weight catalyst per ton substrate	ppm Ru (mg / Kg)
1 st Gen (Noyori)	S/C 100– 2,000/1	20 - 1 Kg	3,000-150
2 nd Gen (Wills)	S/C 1,000-20,000/1	2 Kg – 100 g	300-15



R', R'' = alkyl, aryl, halide, OR, NR₂

- First generation Noyori catalysts have well-understood scope
- Reliable and cost-effective on 'simpler' targets

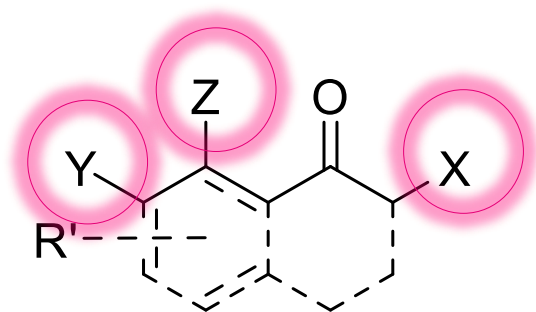
Second generation Wills catalysts offer incremental advantages:

- Much lower loadings
- Easier product purification

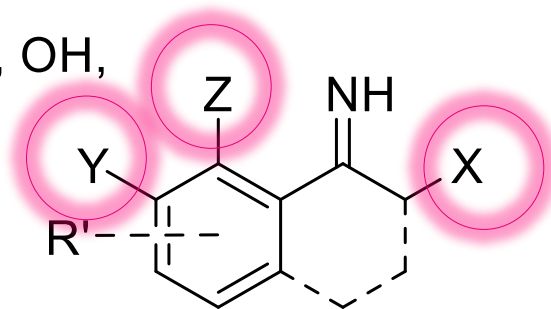
Catalyst loading in transfer hydrogenation

The complex substrates

	Molar catalyst loading	Weight catalyst per ton substrate	ppm Ru (mg / Kg)
1 st Gen (Noyori)	S/C 20 - 100 (if possible at all...)	100 - 20 Kg	15,000-3,000
2 nd Gen (Wills)	S/C 100- 1,000/1	20 - 2 Kg	3,000-300



X,Y,Z = NHR, NR₂, SR, OH,
OR, COOR, CONR₂



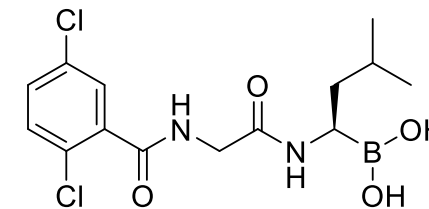
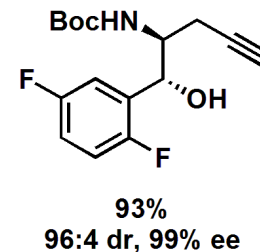
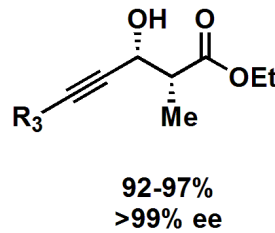
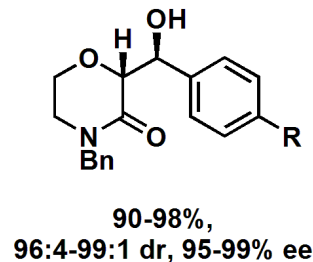
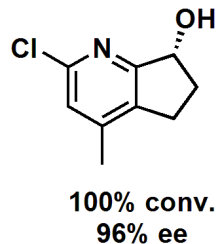
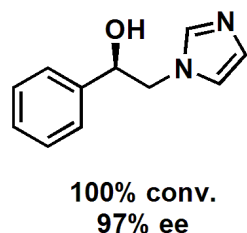
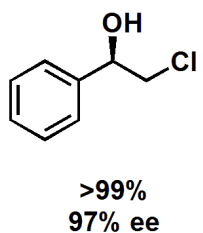
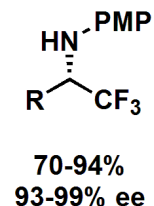
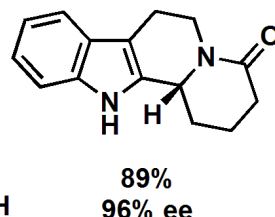
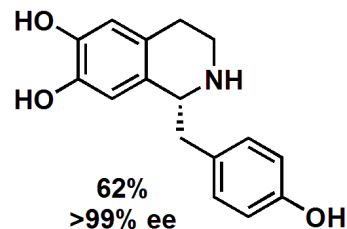
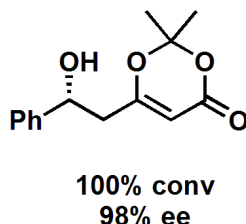
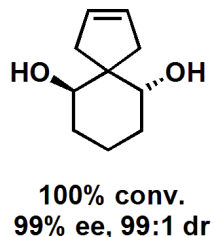
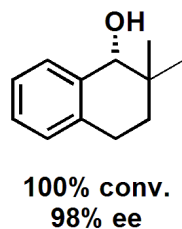
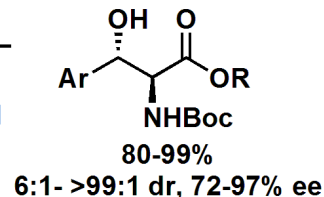
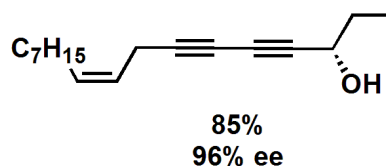
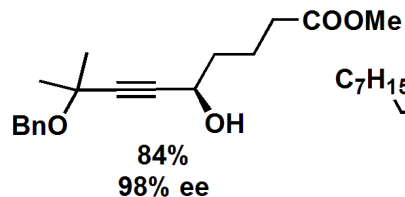
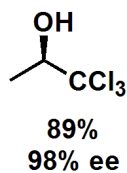
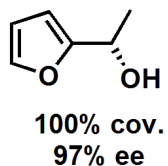
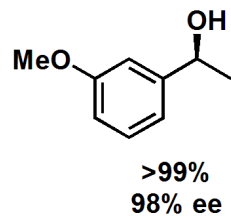
Second generation catalysts:

- provide more robust processes
- enable 'impossible' transformations
- Reduce catalyst loadings

*Assuming MW catalyst = 2 x MW substrate and Ru 1/6 of catalyst MW

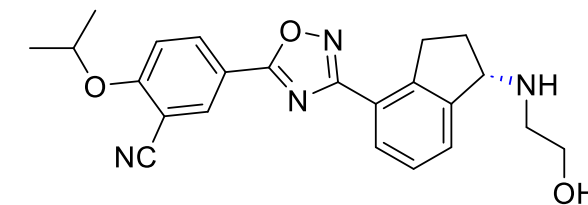
Transfer hydrogenation has a wide scope

Second generation catalysts are effective on complex molecules



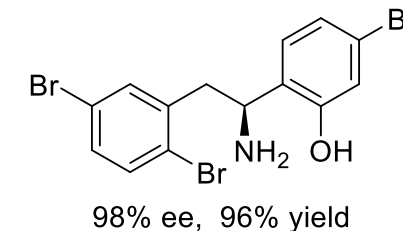
Ixazomib

Sandoz: Chem. Sci.
2022, 13, 2946-2953



Ozanimod

Chemessentia: Eur. J. Org.
Chem. 2021, 2021, 1924



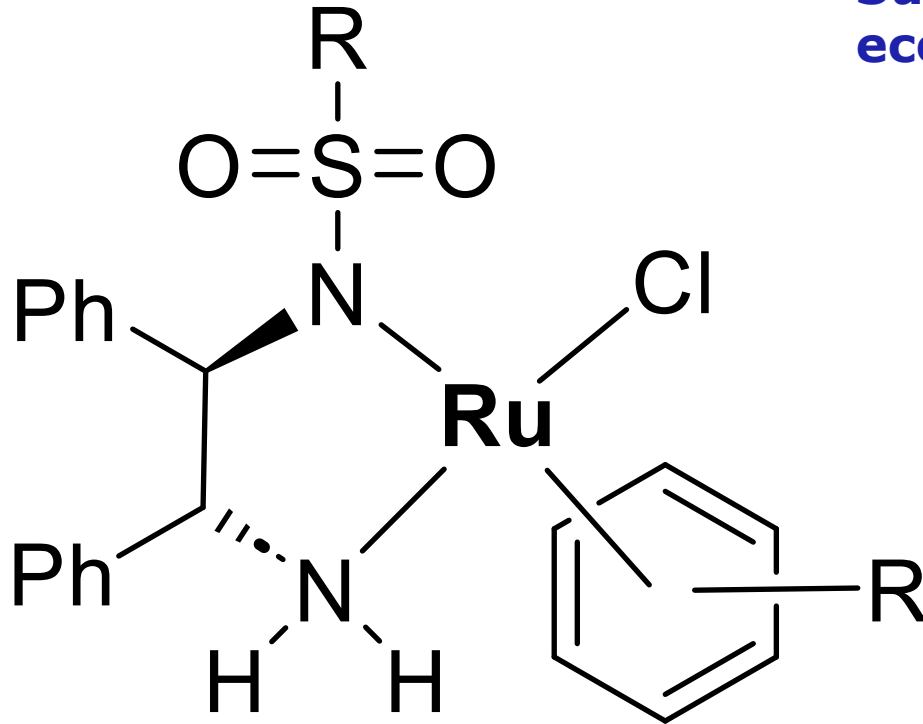
Elbasvir

Merck: Org. Lett. **2014, 16,**
2310

Review: Wills, Nedden, Zanotti *Chemical Records* **2016, 16, 2623**

Carbon footprint of a first-generation TH catalyst

LCA Tools: SimaPro 9.6 (Pre-Sustainability, The Netherlands) with ecoinvent v3.10 (ecoinvent, Switzerland)

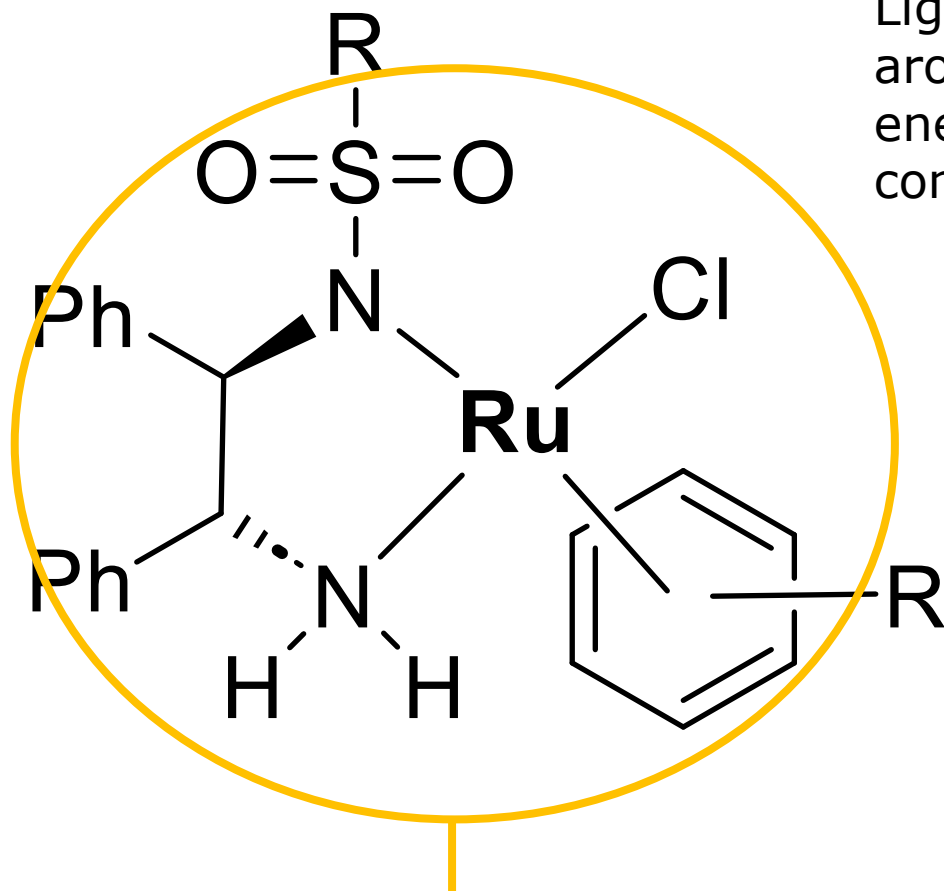


<https://ecoinvent.org/database/ecoinvent/Version3>

Wernet, G., Bauer, C., Steubing, B., Reinhard, J., Moreno-Ruiz, E., and Weidema, B., 2016. The ecoinvent database version 3 (part I): overview and methodology. The International Journal of Life Cycle Assessment, [online] 21(9), pp.1218–1230.

Carbon footprint of a first-generation TH catalyst

DISCLAIMER: this is work in progress !

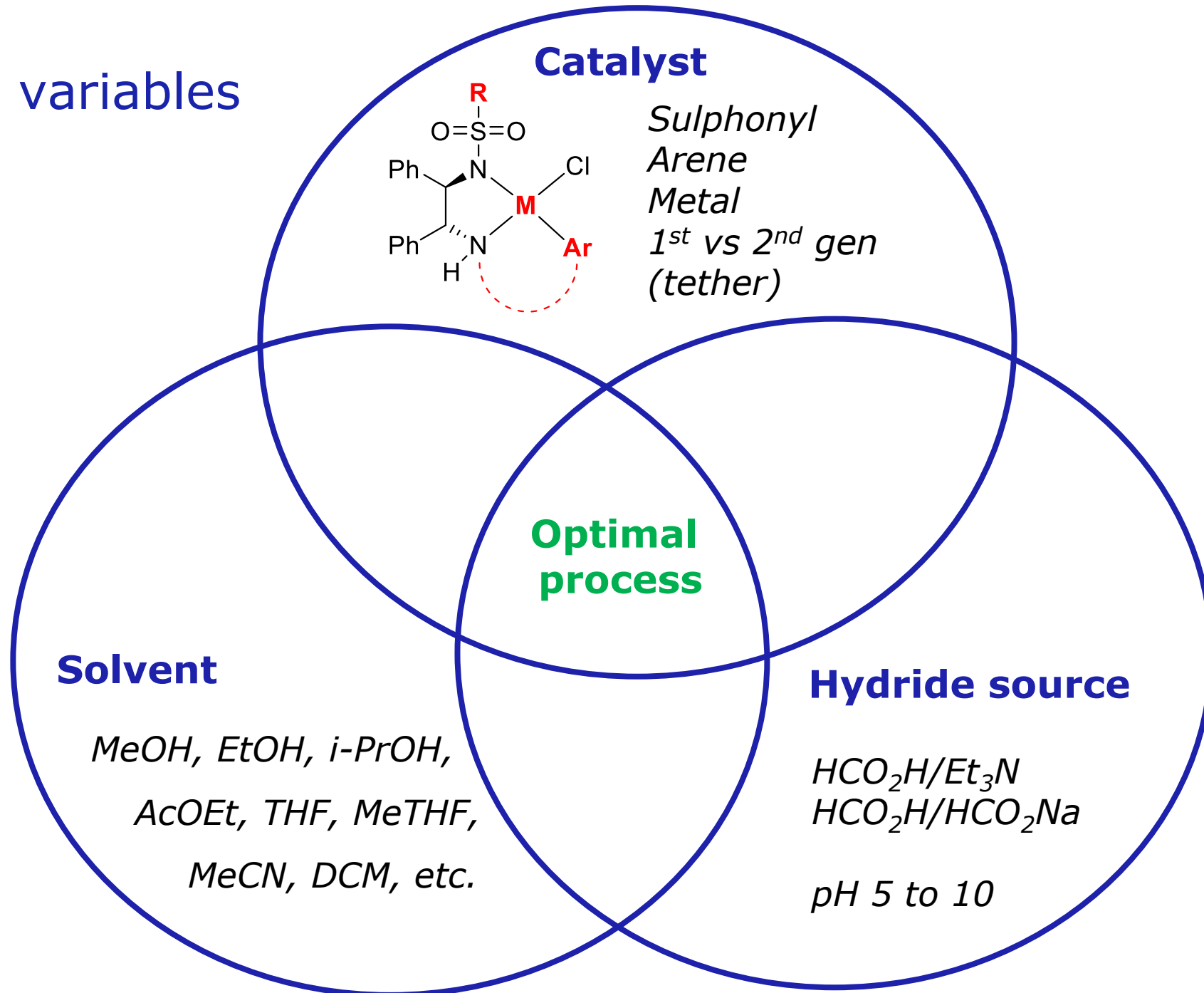


Ligand TsDpen based on *Org. Synth.* **1998**, 9, 387: around $\sim 1,000 \text{ Kg CO}_2 / \text{Kg}$; waste included, and energy not included (solvents biggest contributors).

Estimation based on model Birch reduction : *OPRD* **2024**, 28, 2168 $\sim 100 \text{ Kg CO}_2 / \text{Kg}$ (largely solvent dependent!), waste included, energy not included

Estimated total: $\sim 3,500 \text{ Kg CO}_2 / \text{Kg}$ product, waste included, and energy not included. Metal contribution approx. 70% (assuming Ru 70% from secondary sources)

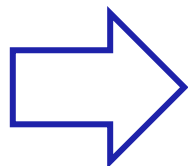
Reaction variables



Optimisation case studies with TH catalysts

From literature conditions to scalable process

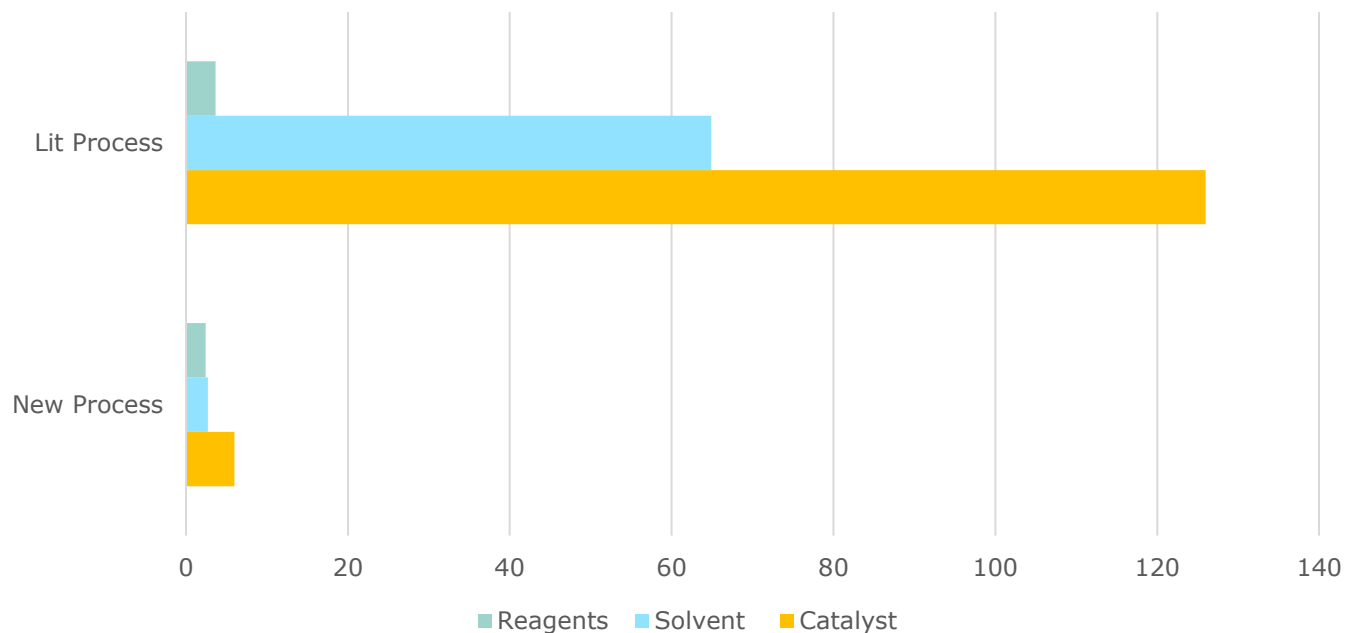
S/C 50/1,
HCOOH/Et₃N 5/2, CH₃CN



1st Gen catalyst,
MeOH/water, 10 eq. NaOOCH

S/C 1,500/1

Estimated footprint of TH step



Catalyst GWP remains major contributor to step but is reduced by 30 times

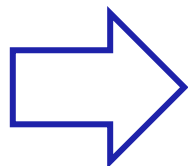
Optimization enables reduction of solvent/reagents impact by a factor of 14 times

No isolation included
No waste disposal included

Optimisation case studies with TH catalysts

From initial conditions to scalable process

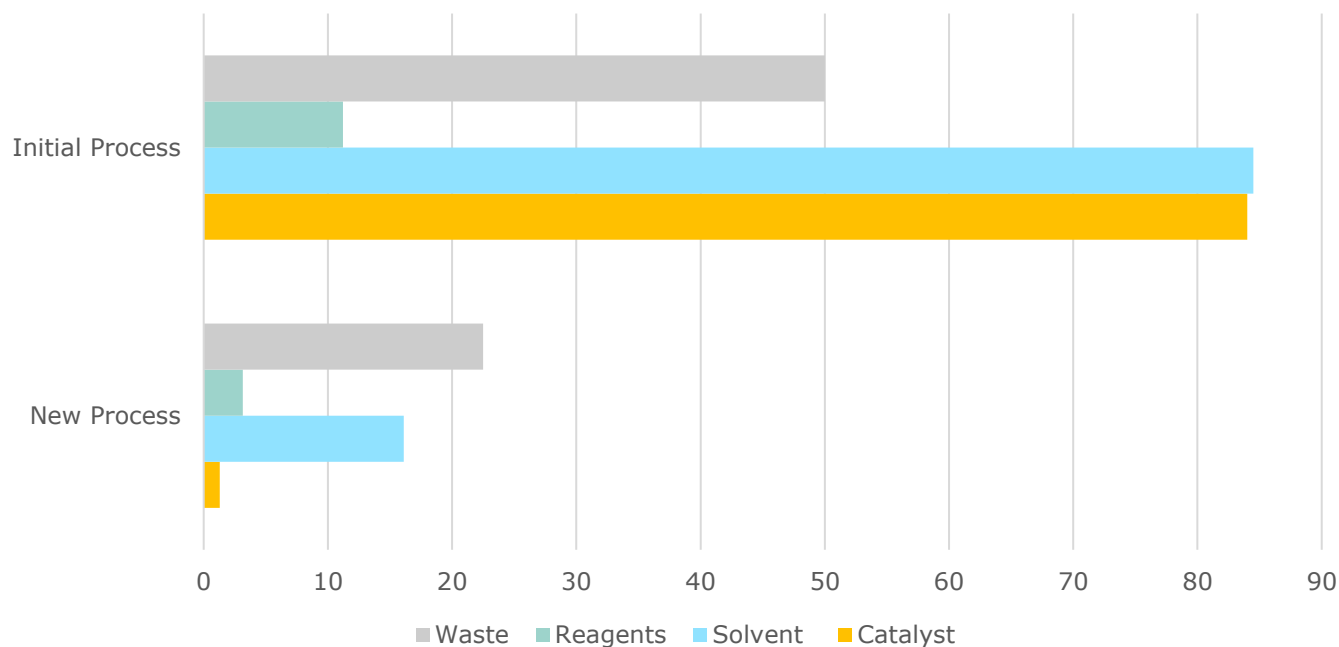
S/C 50/1
HCOOH/Et₃N 1/1, THF



1st Gen catalyst, IPA,
0.1 eq. base, 1.1 eq. HOOCH,

S/C 3,000/1

Estimated footprint of TH process



Semi-optimized isolation and waste disposal included

Catalyst GWP similar to solvent in initial process and negligible in optimized process

Optimization reduced impact of catalyst by a factor of 60 and of combined solvent/reagent/waste by a factor of 3.5

About design for refining

Challenges in closing the metal loop

Process optimization improves costs and sustainability, but metal recovery can be challenging

Low metal concentration

Nature of liquid waste (hazard, toxicity...)

Pretreatments requirements

Representative sampling

Understanding the mass balance – where does the metal escape?

Trade in and out of countries – regulations

Design the process for refining

A closed-loop approach will reduce carbon emission and capital expenditure

It is important to:

- Understand metal balance
- Understand waste pre-treatment

D. Arnold *et al.*

'Designing for refining' submitted to *Chemistry Today*, **2024**

There are solutions to maximise value recovery from liquid waste:

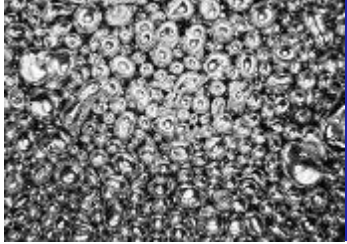


See, for example:

<https://www.mastermeltgroup.com/catalyst-webinar>

Conclusions

PGMs: challenging the myths



They are expensive, it would be better to switch to cheaper alternatives

They are used in small quantities: expensive on a per-gram basis, not on a **total cost contribution** basis. Because of efficiency of use and recycling, using PGMs is often cheaper than alternatives



They are difficult to recycle effectively

Recycling of all PGMs happens routinely & cost-effectively today. If retained in a closed loop, PGM value is retained and can be endlessly reused.



Mining is subject to geopolitical risk & ESG concerns

Mined PGMs from southern African is typically from **highly regulated companies** that report on ESG performance, support local communities and are investing to reduce environmental footprint.



They are scarce metals and there is not enough available

Hydrogen is a replacement market for the PGMs as catalytic converter use declines. JM's PGM market research experts project that hydrogen and fuel cell **market growth can be from existing supplies.**

And my own conclusions...

What matters is not the headline price / carbon footprint but the **economic/sustainability value** that PGMs create

Process optimization unlocks the value of catalysts, enables better use of resources, minimizes contribution of **catalyst cost/footprint**

PGMs are an example of functioning **circular economy** and their future availability is sustainable

(...and I have ignored the comparison with biocatalysis – for discussion another day!...)



JM

Johnson Matthey
Inspiring science, enhancing life

and

Many thanks to:

THANK YOU !

Jane Patrick

Marge Ryan

Tim Murray

Sarah Facchetti

Dan Arnold

Antonio.Zanotti-Gerosa@matthey.com