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Limitations to elemental substitution as exemplified by the platinum-group metals

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1. Substitute review by application

1.1. Catalytic converters

PGMs have been utilized in automotive catalytic converters to reduce emissions from vehicle exhausts since the mid-1970s.[1] Today, under increasingly strict air quality regulations across the world, PGMs are used in the vast majority of both spark-ignition (petrol or gasoline) and compression-ignition (diesel) light-duty vehicles, and increasingly in heavy-duty vehicles and non-road mobile machinery.[1]

Varying combinations of Pt, Pd, and Rh are used in modern catalytic converters, with each metal having an important and distinctive role. Pt and Pd are noted as being equally effective at oxidizing CO and hydrocarbon emissions in spark-ignition vehicles.[2] Pt is, however, less susceptible to poisoning by Pb and sulfur, while Pd has a higher resistance to high-temperature ageing, especially in oxygen-rich conditions, and better performance at lean cold starts.[3] The choice between the two is often based on relative metal prices[2] and the dependency of Pt and Pd supplies on their mineral ore grade ratios. Since the mid-1990s, vehicle manufacturers have partially or completely substituted Pd for the typically more expensive Pt in spark-ignition vehicles.[4] Although many original equipment manufacturers have already made the switch to exclusively use Pd-Rh based catalysts in spark-ignition vehicles, some have not. There thus may be some potential for further substitution in either direction with the decision ultimately resting upon corporate strategy and metal prices. Moreover, there is also the potential for substitution in vehicles that are sold into markets with poor fuel quality that still require the use of Pt due to sulfur poisoning as fuel quality improves.

Thousands of catalyst compositions were investigated during the research and development effort that ultimately led to the use of PGMs in catalytic converters, and research into viable alternatives continues to this day.[3, 5-7] Although catalysts based on oxides of base metals, including CuO and Co_3O_4, exhibit activity for the oxidation of CO, they are typically less active in the oxidation of hydrocarbons and tend to react with the alumina support to form less active species.[3, 5] Ag and Au were also eliminated as potential candidates due to their limited activity and durability.[8] Moreover, both Ag and Au have a Tammann temperature that is below that of the average exhaust gas resulting in lower thermal stability.[2]

With the lowering of sulfur levels in diesel fuel and the increased use of diesel particulate filters, the use of Pd has become possible in diesel oxidation catalysts.[1] Today, up to 25% of Pt can routinely be substituted for by Pd, with new technologies allowing for an increase of that portion to as much as 50% in certain applications.[9] The highly oxidizing environment of the diesel exhaust does, however, convert Pd into a catalytically less-active oxide state, thereby requiring the use of Pt which remains in its catalytically-active metallic form.[1]

A recent review suggests that there are various approaches that may overcome the problems of low-temperature activity and thermal stability associated with using Au-nanoparticle catalysts, especially in lean-burning diesel engines whose exhausts have lower temperatures than those produced by spark-ignition engines.[7] Indeed, a catalyst based on Au-nanoparticles, NS Gold™, has recently become commercially available for use in European diesel vehicles.[7] This catalyst does, however, utilise both Pt and Pd in addition to Au.[7]

At this time there does not seem to be a viable alternative that completely eliminates the use of Pt and Pd in catalytic converters. Similarly, despite various efforts,[10] no viable alternative to Rh in catalytic converters has been found.[8, 11]

1.2. Jewellery and investment

All PGMs, with the exception of Os, find major and minor application in jewellery. Pt, alloyed with various metals including Cu, Co, W, and other PGMs to give it the necessary hardness and wear resistance, is the most important PGM for jewellery applications.[4, 12] In addition to its use as an alloying element in jewellery, Pd is used as a fabrication metal albeit in limited quantities, except in China in recent years.[1] Ru and Ir are the most common hardeners of Pt jewellery, while a thin layer of Rh is sometimes electroplated to provide wear-resistance and reflectivity.[13] Although Os is the most efficient hardener of Pt jewellery it is generally avoided due to the volatility and toxicity of its tetroxide.[13]

In the 1920s, white-Au alloys were developed to substitute for Pt-based alloys in the jewellery industry.[4, 14] These white-Au alloys are based primarily on varying combinations of Au-Cu-Ni-Zn or Au-Pd-Ag alloys with Ni and Pd providing the primary bleaching effect respectively.[14] Each alloy composition has both positive and negative attributes with regard to the most important properties of white-Au jewellery, namely colour and reflectivity, hardness, cold workability performance, liquidus temperature, amenability to soldering or brazing, recyclability, susceptibility to fire cracking, amenability to Rh plating for colour enhancement, resistance to tarnish and corrosion, allergy response, and cost.[15] For example, while Ni-based white-Au alloys are characterized by reasonable tarnishing resistance, amenability for Rh plating, a liquidus temperature less than 1100 °C, and inexpensive alloying constituents, they are typically plagued by poor workability, excessive hardness as cast, susceptibility to fire cracking, and decreased recyclability at high Zn content.[16] Moreover, Ni-based white-Au alloys have decreased in popularity due to the allergic reactions associated with high Ni content.[4, 15] In contrast, Pd-based white-Au alloys are characterized by a number of desirable attributes including low hardness as cast or rolled, superior ductility and cold working properties, ease of soldering or brazing, no susceptibility to fire cracking, good corrosion and tarnish resistance, and ease of recycling.[16] Pd-based white-Au alloys do, however, have high melting temperature, high density, and are comparatively more expensive.[15, 16] A detail analysis comparing several Ni- and Pd-based white-Au alloys is presented in section 2.

Pt and Pd also function as investment media in the form of coins and small and large investment bars.[1] Investment in Pt, Pd, and more recently Rh is also possible in the form of physically-backed exchange traded funds (ETFs).[1] Among the PGMs, Pt is generally regarded as the most attractive investment media.[13] Au and Ag are utilized more extensively in this category and could presumably substitute for PGMs. However, each metal has its own characteristics and if PGM investment instruments were no longer available some PGM investors may opt for industrially-based investment alternatives.

1.3. Chemical applications

PGM use in the chemical industry includes process catalysts used in the production of numerous bulk and fine chemicals, gauzes used in the production of nitric acid, as well as laboratory equipment.[4] It would be impractical to discuss all of the various uses of PGMs in the chemical sector and so the focus will be on several of the more important commercial applications for each PGM.

The largest single use of Pt in this category, constituting roughly 5,600 kg of Pt (43% of this category) globally in 2007, is as catalysts in the cross-linking of silicones.[17] Demand for this application is large in part because Pt is not recovered, as Pt is irretrievably lost in the silicone product during its manufacture.[4] Finding ways to reduce the cost associated with using Pt is therefore of great importance to the silicones industry.[17] Low-Pt technologies that require significantly less Pt have been employed and have reduced overall Pt demand for this application in recent years despite the strong demand for silicones.[1, 17]

In addition to these Pt-catalysed hydrosilylation reactions, there are two other reaction types that have been employed in the silicones industry: solvent-based condensation reactions that typically employ a Sn-based catalyst and peroxide-induced free radical processes.[18] Radiation curing is also used in the cross-linking of silicones, especially in the release liner industry where that technology's market share is expected to increase from 15% in 2008 to 20% by 2015.[17, 18] The free radical-initiated curing technologies were developed in the early 1980s but have gained only modest market share mostly in lower performance applications.[17] Unlike the low-Pt technologies, the free radical-initiated systems do not have the advantage of being drop-in replacements with the existing coating systems, thereby requiring significant capital and operational expenditure for current manufacturers to adopt.[17] The current Pt-based systems also have desirable cure kinetics, as well as regioselectivity and chemoselectivity that result in desirable high-molecular weight polymers.[8]

The production of para-xylene, an important precursor for purified terephthalic acid (PTA) via a Pt isomerization catalyst, is likely the second largest user of Pt in this category. A silica/alumina catalyst without Pt was previously used, but suffered from rapid deactivation requiring frequent regeneration.[19] It also does not convert ethylbenzene to xylenes.[19]

Another major use of Pt in the chemical industry is as contact gauzes, which have been used in the commercial production of nitric acid by ammonia oxidation since the early 1900s.[20] In 2010, approximately 3,580 kg of Pt (26% of this category) was purchased for the production of nitric acid.[1] A significant portion of this demand is used to replace the losses of Pt that occur during production due to abrasion and volatilization.[4] Up to 10% Rh is added to increase the gauzes' strength, reduce Pt losses, and improve selectivity.[4, 21] Since 1968, Pd has been used in a subsequent process in catchment gauzes to reduce the losses of both Pt and Rh, but results in the loss of some 30% of the Pd.[4, 21] Although these additions result in improved process economics, the losses of PGMs still constitute a significant expense that is second only to the ammonia feedstock.[22] Various oxidation catalysts, the most promising of which are based on Co, have been investigated as potential replacements for PGM gauzes.[22] Although these alternatives exhibit high catalytic activity they suffer from rapid deactivation and insufficient nitric oxide selectivity.[21] Lloyd notes that it is unlikely that a better catalyst will be developed to replace Pt-Rh gauzes.[21]

Pd catalysts are generally regarded as the most versatile of PGMs and are thus used in a wide range of chemical processes.[23] The four commercial products that utilize the largest volume of Pd catalysts are hydrogen peroxide, acetaldehyde, vinyl acetate monomer, and purified terephthalic acid (PTA).[12] As mentioned previously, Pd is also used in catchment gauzes to recover Pt and Rh in the production of nitric acid.

Large-scale production of hydrogen peroxide is dominated by the anthraquinone process, with the most common catalyst being Pd.[24] A Raney Ni catalyst was used in the original Riedl–Pfleiderer process, but suffered from rapid deactivation and excessive ring hydrogenation.[24, 25] Catalysts based on amorphous Ni/B have recently gained attention as potential alternatives.[26] There is also increased interest in finding a cleaner method of production that is not based on the anthraquinone process.[24] Alternative methods include primary and secondary alcohol oxidation, electrochemical synthesis, direct synthesis via a noble metal catalyst (namely Au, Pd, or a combination thereof [27]), and photocatalysis, to name a few.[24]

Acetaldehyde is mainly produced via the Wacker-Hoechst process for the liquid-phase oxidation of ethylene using a Pd catalyst.[28] It can also be produced from the partial oxidation of ethyl alcohol over a Ag catalyst, hydration of acetylene via a Hg catalyst, and more recently via the conversion of synthesis gas over a Rh catalyst.[28]

Vinyl acetate can also be produced in various ways. Approximately 80% of available production capacity is used in the reaction of ethylene with acetic acid and oxygen in the gas phase with a heterogeneous catalyst containing Pd.[29] The remaining 20% of production capacity is produced via the addition of acetic acid to acetylene in the gas phase over a heterogeneous catalyst containing Zn salts.[29] The former process was previously conducted in the liquid phase using homogenous Pd/Cu salt catalysts, while the latter process was previously carried out in the liquid phase in the presence of homogenous Hg salt catalysts.[29] Another previously utilized route involved the addition of acetic anhydride to acetaldehyde, while a process involving the reaction of methyl acetate or dimethyl ether with carbon monoxide and hydrogen using Rh (or another PGM) homogeneous catalyst is thought to be developed to, but not yet utilized at, an industrial level.[29]

Several catalysts including those based on Ni and all six PGMs have been investigated in the hydropurification of crude terephthalic acid, but none have been as successful as Pd catalysts.[30] The use of a bimetallic Pd-Ru catalyst does show some promise but, obviously, does not eliminate the need for Pd in this application.[30] On the other hand, nitric acid can be produced without Pd catchment gauzes, but at the expense of Pt and Rh.[4]

After Pd, Rh is the second most active PGM for the hydrogenation of alkynes and alkenes to alkanes, but Ni and Ni/Mo catalysts are also commercially available.[23]

Rh catalysts are utilized in the oxo process for the conversion of alkenes to n-aldehydes (hydroformylation), carbonylation of methanol to acetic acid (Monsanto process), carbonylation of methyl acetate or dimethyl ether to acetic anhydride (Hoechst/Halcon process), and as previously mentioned, with Pt in the catalytic oxidation of ammonia.[12] A Co-based catalyst, which the Rh-based catalyst replaced, can substitute for Rh in the oxo process.[12, 31] Also, a Co/iodine catalyst or a promoted Ir/iodide catalyst could substitute for the Rh/iodine catalyst used in the Monsanto acetic acid process.[12] The Co/iodine catalyst is, however, significantly less active than the Rh catalyst.[12] Nitric acid production can be carried out using Pt-only gauzes, but would result in lower reaction yields, higher Pt losses, decreased gauze strength, and shorter catalyst life.[32, 33] Hydrogen cyanide can be produced with Pt-Ir catalysts instead of Pt-Rh catalysts.[34] After Rh, Ru is the second most active PGM catalyst for the hydrogenation of aromatic rings.[23]

Ru catalysts are utilized in hydrogenation, oxidation, hydrogenolysis, synthesis of ammonia, synthesis of hydrocarbons, and hydroformylation.[12] The KBR Advanced Ammonia Process (KAAP™), which uses a Ru catalyst, is thought to be 20 times more active than the process that utilizes a magnetite-based catalyst.[35] The magnetite catalyst is still used, however, in the majority of ammonia synthesis plants.[12] The water gas shift reaction can also be carried out using Fe-based catalysts instead of those based on Ru.[36] Hydrogenation of aliphatic aldehydes is traditionally performed with a Ni catalyst, but Ru has several advantages including lower operating temperature and pressure making it the preferred metal.[23]

Ir catalysts are used in hydrogenation, acetic acid synthesis, and hydroformylation.[12] As previously mentioned, the Rh-based catalyst used in the Monsanto acetic acid production process can substitute for the promoted (typically with Ru) Ir-based catalyst used in the Cativa™ process.[12, 37] The Ir-based catalyst does, however, allow for higher reaction rates and can tolerate a wider range of process conditions.[12, 37] In other reactions, Rh or other PGMs can often substitute for Ir.[23]

Os catalysts are used in a limited number of chemical processes, the most important of which is in the syn-dihydroxylation of alkenes.[12] In this reaction, RuO_4 is the next most commonly used complex after OsO_4.[38] Numerous other methods using different reagents have also been investigated.[38] Other applications of Os include oxidation of alcohols to aldehydes, ketones, or carboxylic acids, hydrogenation of olefins, α, β-unsaturated carbonyl compounds, and carbon monoxide, and the water gas shift reaction.[39] Ru- and Fe-based catalysts are, however, more favourable to Os in the water gas shift reaction.[36]

Although several possible alternatives have been outlined here there is often little incentive to substitute base metals for PGMs because PGMs are often more catalytically active, operate under milder reaction conditions, are non-toxic and non-pyrophoric, and do not require pre-treatment.[12] PGMs are also recovered and recycled with high efficiency[4, 40] making substitution desirable only in applications in which significant PGM losses occur (e.g., silicones and nitric acid production). There are other considerations that may also disincentivise substitutions. Plant or process modifications may, for example, be necessary thereby requiring significant capital expenditure.[41] In other cases, a change in catalyst may require the use of a more expensive ligand thereby making the substitution uneconomical.[8]

1.4. Petroleum refining applications

PGMs are used in several large-scale petroleum refining operations, the most important of which are catalytic reforming and isomerization.[12] Furthermore, Pd catalysts are used in hydrocracking,[4] while Pt catalysts are also used in the production of certain biofuels.[1]

In catalytic reforming, Pt is used with promoters, namely Re, Ir, or Sn, to significantly improve process performance.[42] The use of these metals reduces but does not eliminate the need for Pt. Catalysts based on oxides of Mo were used in the older hydroforming process but were not as active or as selective and required frequent regeneration.[6] The markedly lower performance of these alternatives and the efficient recycling of the Pt catalysts make substitution impractical. Moreover, it is unfeasible to use the Mo-based catalysts in the existing reforming units.[6] It is therefore not surprising that demand for this category exhibits low price elasticity and then only after substantial lags.[5] The non-Pt catalysts are, however, widely used in a regenerative process for sulfur-rich feeds that would otherwise poison the Pt catalysts if pre-treatment (hydrodesulfurization) processes are not employed.[43] Thermal reforming is an alternative but is less effective and less economical than catalytic reforming.[44]

Three types of catalysts are commercially available for light naphtha isomerization: zeolitic, chlorided alumina, and sulphated zirconia.[45] A wide range of base metals and all six PGMs have been investigated as potential promoters of sulphated zirconia catalysts.[46] However, all commercial catalysts utilize Pt due to its superior activity, stability, and sulfur tolerance.[45, 46] Furthermore, while both Ni and Pt catalysts are used in the benzene saturation process, Pt catalysts are recommended.[45]

In hydrocracking, combinations of Ni, Mo, and W may be used instead of Pd catalysts.[44] However, Ni catalysts seem to be less tolerant of the sulfur and more sensitive to the nitrogen content of the feedstock.[47] Finally, in hydrotreating, Ni, Co, and Fe are among the wide variety of metals that can be used instead of Pd and Pt as hydrogenation catalysts.[44]

1.5. Glass applications

High melting point, oxidation and corrosion resistance, high mechanical strength at extreme high temperatures, good ductility, formability, and weldability, as well as the capability for extremely efficient recycling are several of the advantageous properties that make PGMs ideally suited for constructing equipment used in the manufacture of various technical, specialty, and optical glass.[48] Specifically, Pt is used in self-supporting parts, linings, thin-layer coatings on ceramic substrates in the form of bushing troughs, perforated plates, stirrers, and plungers, to name a few.[4, 49] Rh is added as an alloying agent in some applications to raise the melting point and increase strength and stability.[13] The amount of Rh used in these applications is partly dependent of the price ratio of Pt to Rh, with increases in the price of Rh relative to Pt resulting in decreased use of Rh.[13] The extent to which this can be done is, however, limited to 5 – 20% Rh, with the exception of optical glass used to manufacture liquid crystal displays (LCDs) in which no Rh is used due to its causing discoloration of the product.[4] The short time period (1-2 years) between refurbishments provides manufacturers with the opportunity to make changes quickly. However, the percentage of Rh used in the manufacture of LCD glass has remained relatively stable.

The only other alloying elements that can be considered are Au and Ir because they do not significantly reduce the chemical stability of the Pt.[48, 49] Recent developments have also allowed for Ir-based fabrications and linings although some limitations still exist.[49, 50] Ir is more likely to complement rather than substitute for Pt-Rh technology.[49, 50] Anecdotal evidence suggests that there are some companies, mainly in China, that are thought to have added Pd in place of Rh in small amounts. The lack of available alternatives is again highlighted in the extreme price inelasticity of demand for this category.[51]

1.6. Dental, medical, and biomedical applications

Pd is utilized as both a fabrication metal and an alloying element in over 90% of precious metal alloys used in dentistry, while Pt is used exclusively as an alloying element in precious metal alloys.[4] In general, precious metal alloys fall into three categories: high-Au alloys, Au-reduced alloys, and Pd-alloys.[4] Aside from these precious metal alloys, there are non-precious metal alloys based on Ni-Cr and Co-Cr as well as ceramics that are increasingly being used.[4, 52] PGM-based alloys are thus vulnerable to substitution by non-precious metal alternatives in certain price environments. Precious metal alloys are often, however, the preferred material for permanent tooth replacement.[4] Moreover, in Japan, government subsidies for dental work specify the use of a Pd-Au alloy (kinpala), thereby limiting the incentive for substitution.[1]

Dental alloys constitute less than a quarter of the Pt demand in this category at roughly 1,700 kg in 2010, down from 3,700 kg in 2005.[1] Biomedical devices and components now represent the largest share in this category at approximately 5,400 kg of Pt in 2010, up from 3,100 kg in 2005, while anticancer drugs comprise a small portion at approximately 800 kg per year.[1] Pt use in biomedical devices includes guide wires, catheters, pacemakers, and defibrillators.[1] Pd is emerging as an alternative to Pt in certain medical device applications,[53] while non-Pt based anticancer drugs include organometallic compounds that utilise Ru, Os, Rh, Co, Fe, Au, and Ga.[54]

The use of the other PGMs in this category is often limited to that of alloying agents. For example, Ru and Ir are used as alloying agents in dental applications, while Ir is alloyed with Pt in pacemakers and catheters.[1] OsO_4 and RuO_4 are also used as staining agents in electron microscopy.[12, 55]

1.7. Electrical and electronic applications

Pd and Ru are the two most widely used PGMs with respect to electrical and electronic applications, while Pt also plays an important role in several applications.[12]

Pd is used mainly in thick film pastes in multilayer ceramic capacitors (MLCC), conductive tracks in hybrid integrated circuits (HIC), and in plating of connectors and lead-frames.[12] The use of Pd and Pd-Ag alloys in MLCC is its largest electronic application constituting more than half of the Pd demand in this category in 2007.[1] The introduction of Ni- and Cu-based MLCC in the mid-1990s has, however, steadily eroded the market share of Pd-based MLCCs from approximately 85% in 1997 to 10-15% in the late 2000s.[1] In recent years, an overall increase in MLCC demand has not been sufficient to offset the decrease of Pd use due to this substitution and "thrifting" via miniaturization.[1] Pd-based MLCC have thus been largely confined to niche areas, including military and aerospace applications.[1] Because substitution has already occurred, further substitution of Pd with base metals, while still possible, will likely be considerably slower.

Pd also competes with base metals in HIC, but less so due to its performance advantages.[1, 12] Pd competes with Au in other electronic applications including plating for connectors and circuit boards, with the choice often being based on price.[1] The international move to phase out Pb-based solders has furthered the use of Pd which helps maintain reliability at the high temperatures required for Pb-free plating and soldering.[1]

Ru is used in thick film pastes in chip resistors and conductive pastes in plasma panel displays.[1, 32] Ru largely displaced the previously used thick film resistors based on combinations of Ag, Pd, and their oxides,[56] although Pd continues to be used in low-Ohmic resistors. While stable oxides of other PGMs (e.g., Rh, Ir, and Os) have previously been noted as potential alternatives to Ru oxide,[56] none pose a threat to Ru's commercial dominance in this application. In contrast, Ru incorporated in photoimageable thick-film pastes used in plasma display panels have largely been replaced by non-precious metal alternatives (e.g., DuPont™ Fodel® 8G Thick Film Paste).[1] Other precious metals (e.g., Pd, Ag, and Rh) can be used in reed contacts.[32]

Hard disk drives (HDDs) have become an increasingly important application for both Ru and Pt in recent years. Both metals were used in longitudinal magnetic recording (LMR) and are currently used in the perpendicular magnetic recording (PMR) technology that has largely superseded LMR. In 2009, approximately 3,000 kg of Pt was purchased for use in HDDs, where it is sputtered onto disks as a CoCrPt-oxide alloy.[1] As demand for higher areal densities continues, other recording media will be needed. Among the current options are patterned recording and heat-assisted magnetic recording technologies based on $L1_0$-ordered phases of FePt, FePd, CoPt, and MnAl, Co/Pt, Co/Pd, and Co/Ni multilayers, and those utilizing rare earth elements ($SmCo_5$ and $Nd_2Fe_{14}B$).[57-59]

Ru is used in the intermediate layers in PMR technology to reduce signal noise by decoupling the soft magnetic underlayer and the recording layer.[57] Intermediate layers based on other PGMs, including IrMn, have been investigated as potential alternatives to Ru.[60-63]

Solid-state drives (SSDs), which do not utilize PGMs, are a technology-level substitute that competes with HDDs in desktop and laptop personal computers. SSDs have several performance advantages but, despite continued reductions in price, are still more expensive per unit of storage and thus HDDs are likely to remain in demand for larger data storage requirements including cloud computing.[64]

Thermocouples are likely the second largest application of Pt in this category, accounting for roughly 20% of this category's demand.[65] This demand, however, fluctuates with the production cycles of the glass, steel, and semiconductor industries in which the Pt-Rh thermocouples are used for high temperature precision measurements.[12, 13, 65] Type K (Ni-Cr vs. Ni-Al) and Type N (Ni-Cr-Si vs. Ni-Si-Mg) thermocouples can be used in oxidizing or inert atmospheres up to 1260 °C,[66] while W-Re thermocouples may be also a possible substitute for Pt-Rh in the steel industry.[67] Other PGM thermocouples include Ir vs. Ir-Rh thermocouples that may be used for very high temperature applications but generally suffer from poor mechanical properties, short lifetimes, and unstable emf versus temperature characteristics.[68] Additionally, Rh-Fe thermocouples can be used for precise temperature measurement under 40K.[4]

Other electronic uses of Pt include varistors and bond wires, while other electrical uses of Pd and Rh include contact materials such as switches, relays, and sliding and pressure contacts.[4] Fuel cells are also included in this category, but remain relatively minor at roughly 600 kg of Pt in 2010.[1]

The use of Ir by the electronics industry is in the form of crucibles used for growing high purity single crystals of metal oxides.[12] Although a number of different crucible materials exist, only a few can substitute for Ir in this application. Pt and Rh, for example, can only be used in medium temperature ranges, while high melting point materials such as Mo, Ta, W, and graphite can only be used in reducing or neutral atmospheres.[69, 70] That said, Mo and W crucibles can be used to grow sapphire (Al_2O_3)[71, 72] and yttrium aluminium garnet (YAG) crystals.[73] Ir is often, however, the preferred crucible material for growing a number of high purity single crystals, including lutetium oxyorthosilicate (LSO), gadolinium oxyorthosilicate (GSO), and gadolinium gallium garnet (GGG).[74]

1.8. Electrochemical applications

PGMs also play an important role in several electrochemical applications, including cathodic protection, electrogalvanizing, electrowinning, and in the chlor-alkali industry.[12] In the latter, dimensionally stable anodes (DSAs) based on a titania substrates coated with oxides of Ru and Ir are used in the electrolysis of brine to produce sodium hydroxide and chlorine.[1] In the early 1900s, Pt or magnetite anodes were used, but Pt use was cost prohibitive and the magnetite suffered from limited current density.[75] Graphite anodes were then introduced and used exclusively in chlorine production for more than 60 years before being replaced in the 1970s and 1980s by noble metal oxide coatings on titanium substrates that had the advantage of lower power consumption.[76, 77]

Three electrolytic cell designs are used to produce the majority of chlorine worldwide: diaphragm, mercury, and membrane cells.[13] In 2000, 42% of chlorine manufacturing capacity used the diaphragm technology, while 33% and 19% utilized membrane and mercury technologies, respectively, with the remainder being obtained mostly from the electrolysis of hydrochloric acid (2%) and potassium chloride (3%).[77] Today only membrane technology plants are constructed, while mercury and diaphragm technologies are slowly being replaced in a global trend towards membrane technology adoption.[1] While the diaphragm technology utilizes anodes coated with Ru, the membrane technology utilizes ones based on a mixture of oxides of Ru and Ir.[1] Previously, Ru and Ru-Sn coatings were used in the membrane cells but were prone to degradation via Ru losses, resulting in a short operating life of 2-3 years.[77] Thousands of other anode compositions have been patented, but few are believed to be commercially successful.[75] For example, Co oxide coatings were developed by Dow Chemical up to a semi-commercial state, but proved inferior to those of PGM oxides.[76]

1.9. Other applications

PGMs are also used in a wide range of other applications that are too numerous to recount in detail here. Some of the more prominent uses include automotive spark plugs and oxygen sensors, stationary pollution control, coatings of turbine blades, as well as cathodic protection for marine vessels, deep-sea oil-drilling platforms, and piping in petroleum refining and geothermal energy industries.[1, 76] PGMs can often substitute for each other in these applications. For example, either Pt or Ir can be used in spark plugs.[78]

2. Multi-Attribute Vector Distance

It is sometimes necessary to compare potential substitutes across multiple, often competing, attributes. The multi-attribute vector distance (MAVD) metric, presented in equation (1) below, was derived to perform such a calculation by measuring the Euclidean distance between a substitute's attribute value and the optimal or target value across the multiple attributes of interest.

$$MAVD = \sqrt{\sum_i \alpha_i \left(A_i - A_i^T\right)^2} \qquad (1)$$

The following example illustrates the use of the MAVD metric by comparing different Ni- and Pd-based white-Au jewellery alloys along three attributes: colour difference (DE), liquidus temperature, and Vickers hardness (HV). Values for these three attributes for 21 different alloy compositions are noted in Table S1 based on data reported by Normandeau and Roeterink.[15]

Table S1 Comparison of various Ni- and Pd-based white-Au jewellery alloys

Alloy category	**Gold content** (carats)	**#**	**Alloy composition (%)**									**Attributes**			**MAVD**
			Co	Ni	Cu	Zn	Pd	Ag	In	Sn	Au	**Colour difference** (DE)	**Liquidus temperature** (°C)	**Vickers Harness** (HV)	
Ni-based white-Au alloys	10	1		10.3	37.0	11.0					41.7	5.9	1042	120	**84**
		2		12.4	41.6	4.3					41.7	5.6	1028	133	**68**
		3		13.9	36.4	8.1					41.7	6.5	1018	141	**59**
		4		19.2	32.1	7.1					41.7	4.5	1087	147	**128**
		5		20.0	25.2	13.1					41.7	2.9	1049	163	**93**
	14	6		7.2	26.4	8.1					58.3	7.1	994	128	**35**
		7		8.9	29.7	3.1					58.3	6.9	995	151	**39**
		8		9.9	26.0	5.8					58.3	6.5	994	155	**40**
		9		10.4	24.4	6.9					58.3	6.2	977	143	**20**
		10		13.7	21.7	6.2					58.3	5.3	995	160	**43**
		11		14.0	18.0	9.7					58.3	3.9	981	164	**36**
	18	12		13.5	8.5	3.0					75.0	6.5	960	235	**100**
Pd-based white-Au alloys	10	13			20.5	1.4	28.0	8.4			41.4	3.5	1091	161	**134**
	14	14			21.7		20.0				58.3	2.3	1100	172	**145**
		15			14.7		20.0	7.0			58.3	4.8	1115	160	**157**
		16			14.7	2.0	20.0	5.0			58.3	3.2	1075	178	**123**
		17			14.7		20.0	5.0	2.0		58.3	6.2	1092	165	**136**
		18			14.7		20.0	5.0		2.0	58.3	7.3	1077	175	**124**
		19	2.0		15.0		20.0	5.0			58.3	9.3	1105	167	**149**
		20			14.7	1.0	20.0	6.0			58.3	3.2	1094	161	**137**
	18	21			7.0	3.0	15.0				75.0	4.3	1074	167	**118**

2.1. Target values

The colour difference (DE) metric is actually a vector distance measurement (similar to the MAVD) that is based on the Euclidean distance along the three colour coordinates (red/green (a*), blue/yellow (b*), and luminance (L*)) utilized by the CIE (International Commission on Illumination) colour measurement system.[14, 15] The values noted in Table S1 are calibrated against a 95%Pt 5% Co jewellery alloy standard.[15] The target value is thus zero.

In addition to colour matching, Normandeau notes that another primary requirement for commercial white-Au alloys is a liquidus temperature that is suitable for conventional manufacturing techniques, which he arbitrarily sets at below 1100 °C.[16] In this analysis a target liquidus temperature is set at 960°C to match the lowest reported value among the 21 alloys analysed.

With respect to Vickers hardness (HV), values above 200 are considered undesirable because such high HV values are usually accompanied by increased difficulty in fabrication.[15] O'Connor suggests that an HV value between 120 and 150 is preferred,[79] while Normandeau and Roeterink suggest that a value between 140 and 180 HV ensures adequate wear resistance for jewellery.[15] A value of 135 HV, which is the HV value for the 95% Pt 5% Co jewellery alloy,[80] is selected as the target in this analysis.

2.2. Results and discussion

The MAVD values for the 21 alloys are reported in the last column of Table S1. These results suggest that, based on the three attributes investigated, alloy #9, followed by alloys 6 and 11, is the closest match to the selected target values. Overall, the 14-carat Ni-based white-Au compositions have the lowest MAVD values. The other compositions performed less-well mainly because of their higher liquidus temperature.

It is important to note that in this analysis each of the three attributes was weighted equally (i.e., $\alpha_{DE} = \alpha_{Liquidus\,Temp.} = \alpha_{HV} = 1$). This rather arbitrary weighting assumes that a 1°C change in liquidus temperature is equivalent in preference to a 1-point change in DE and a 1-point change in HV. Alternative weightings can be introduced to allow for a more appropriate accounting of the relative importance of the attributes and may result in different conclusions regarding which alloy is the most suitable. Alternatively, or in conjunction, an analyst may choose to normalize each of the attributes so as to perform a relative comparison. Equation 2 below is an alternative formulation of the MAVD metric in which each attribute is normalized by the target value.

$$MAVD = \sqrt{\sum_i \alpha_i \left(\frac{A_i - A_i^T}{A_i^T} \right)^2} \qquad (2)$$

Finally, it is important to remember that the analysis performed here utilized only three attributes and that there are other important quantitative attributes of jewellery alloys such as ultimate tensile strength (UTS), yield strength (YS), and % elongation that could be included as well. Similarly, non-quantitative metrics such as the fire-cracking resistance and nickel allergy (DMG spot) tests, which are reported on a pass/fail basis, could potentially be included via a binary format (e.g., 1 for fail, 0 for pass).

Overall, this example illustrates that the MAVD can be utilized to compare potential substitutes across multiple attributes and that it can be modified to suit the needs of the analyst.

3. Price elasticity of demand

As noted in the main text of the article, applications in which demand is relatively elastic infers the availability of adequate substitutes (i.e., if the price of the metal increases its demand in that application decreases at a greater rate because its users are able switch to substitutes), while inelastic demand for an application suggests a lack of suitable substitutes (i.e., if the price of the metal increases its demand in that application decreases at a lower rate due to the lack of adequate substitutes). Similarly, a positive cross-price elasticity suggests that the material is a possible substitute, while a negative value suggests that the material is potentially a complement.

Estimates for price elasticity of demand for some Pt applications found in the literature (e.g., refs [5, 51, 81]) are reported in the following table. These values suggest that Pt demand is relatively inelastic for all major applications, especially glass manufacturing equipment.

Table S2 Price elasticity of demand for Pt found in the literature

Application	Subcategory	Alonso [51]	Charles River Associates [5]	TIAX [81]
Automotive		-0.1		
Jewellery		-0.55		-0.33 (short-run), -0.636 (long-run)
Electrical & electronics	Telephone switches	-0.05	-0.12	
	All other		-0.32	
Chemical	Nitric acid	-0.42	-0.44	
	Other		-0.005	
Petroleum	Reforming	-0.475	-0.05	
	Cracking		-0.51	
Glass		-0.05	-0.045	
Dental and medical			-2.8	
Other		-1		
Overall Pt			-0.03	-0.344 (short-run), -1.15 (long-run)

To supplement and update these values, price elasticity estimates for several Pt and Pd applications have been derived via regression analyses using time-series data with the following generic equation:

$$\ln D_{t,i} = \alpha + \beta_{P,i} \ln P_t + \sum_j \left(\beta_{j,i} \ln X_{j,i}\right) + \varepsilon_t \qquad (3)$$

where $D_{t,i}$ is the demand for a specific metal in application i during time period t, α is a constant representing demand for the metal in said application when all other parameters are zero, $\beta_{P,i}$ is the price elasticity of demand for application i, P_t is the price of the metal during time period t, $\sum_j \left(\beta_{j,i} \ln X_{j,i}\right)$ is the sum of the contributions of all other statistically-significant explanatory variables, and ε_t is the error term.

Historical global demand data were obtained from Johnson Matthey.[1] Data sources for the other variables[a] are noted in the following table along with an indication of whether or not the parameter in question was found to be statistically significant (at three different *p* values).

[a] In addition to the variables noted in the Table S3, several other explanatory variables including motor vehicle production, hard disk drive shipments, and mobile phone subscriptions were attempted in the regression analyses. Although some of these variables were found to be statistically significant the parameters noted in Table S3 were found to be better predictors.

Table S3 Variables and data sources for econometric analysis

	Metal price, constant 1998 US$									Previous year global demand	Global GDP, constant 2005 US$	Global petroleum refinery output
	Pt	Pd	Rh	Ru	Ir	Au	Ni	Co	Mo			
Data source	Johnson Matthey [82] U.S. Geological Survey [83]					Kelly and Matos [84]				Johnson Matthey [1]	World Bank [85]	U.S. Energy Information Agency [86]
Pt analysis												
Autocatalyst	-	++	-								+++	
Chemical	+++	-	-	-	+++	+++	-	-	+++	+++	+++	
Electrical	++	+	-	-						+++		
Glass	-		-		-	-				+++	+	
Investment	+++	-				+++					+	
Jewellery	+++	+++				+++	+++				+++	
Petroleum	+								-		++	+++
Other	+	+++								+++		
Overall	+++	-	-	-	-	-	-	-	-	+++	+++	
Pd analysis												
Autocatalyst	++		+							+++	+++	
Chemical	-	-	-	-	-	-	+	-	-		+++	
Dental	-	+++				-	++	-		+++	-	
Electrical		++					-			+++		
Investment	-	+++				++				+++	++	
Jewellery	-	+					+++			-		
Other	+++	-	+++	-	+++	-	-	-	+++		+++	
Overall	+++		-	-	-	-	-	-	-		+++	

Legend
+++ : $p \leq 0.01$
++ : $0.01 < p \leq 0.05$
+ : $0.05 < p \leq 0.1$
– : $p > 0.1$

A summary of the price elasticity and cross-price elasticity estimates along with details regarding the regression analyses are provided in the following tables. Note that for some applications the metal's price was not found to be statistically significant and thus the price elasticity of demand for those applications could not be determined from the time-series data. This suggests that price elasticity is not constant over time or that there are other factors that are more dominant than price (e.g., regulations require the use of autocatalysts).

Overall, the price elasticity estimates suggest that demand for both Pt and Pd is price inelastic in all applications with the exception of the investment category. Excluding the investment category, jewellery was found to be the most sensitive to prices, which suggests that potential substitutes exist for Pt and Pd jewellery. In general, these results are similar to the results found in the literature (Table S2).

From the cross-price elasticity estimates one finds that Pd is a complement (rather than a substitute) to Pt in autocatalysts and, similarly, Pt and Rh are complements to Pd in the same application. This is indicated by the negative values for the cross-price elasticity estimates. Furthermore, Pd and Ni are noted as being substitutes to Pt jewellery and Au is noted as being a substitute for Pt and Pd in the investment category as indicated by the positive cross-price elasticity estimates. These results are not surprising and affirm the conclusions of the literature review.

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Table S4 Summary of price elasticity and cross-price elasticity for several Pt and Pd applications

	Price elasticity of demand	**Cross-price elasticity of demand** (substitute noted in brackets)
Pt summary		
Autocatalyst	—	-0.18 (Pd)
Chemical	-0.32	0.13 (Ir), 0.17 (Mo)
Electrical	-0.20	0.13 (Pd)
Glass	—	—
Investment	-2.68	2.93 (Au)
Jewellery	-0.70	0.21 (Pd), 0.21 (Ni)
Petroleum	-0.45	—
Other	-0.19	0.27 (Pd)
Overall	-0.10	—
Pd summary		
Autocatalyst	—	-0.29 (Pt), -0.11 (Rh)
Chemical	—	0.11 (Ni)
Dental	-0.16	-0.08 (Ni)
Electrical	-0.19	—
Investment	-1.84	1.58 (Au)
Jewellery	-0.63	0.89 (Ni)
Other	—	-0.63 (Pt), -0.34 (Rh), 0.35 (Ir), 0.68 (Mo)
Overall	—	-0.30 (Pt)

Table S5 Summary of regression analysis for Pt autocatalyst

Regression Statistics	
Multiple R	0.968
R Square	0.937
Adjusted R Square	0.933
Standard Error	0.174
Observations	38

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	2	15.63	7.81	258.94	1.06E-21
Residual	35	1.06	0.03		
Total	37	16.68			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-57.44	2.92	-19.65	1.74E-20	-63.37	-51.50
Ln World GDP (constant 2005US$)	2.11	0.10	21.43	1.05E-21	1.91	2.31
Ln Pd price (constant 1998 US$)	-0.18	0.07	-2.64	0.012	-0.32	-0.04

Table S6 Summary of regression analysis for Pt chemical

Regression Statistics	
Multiple R	0.919
R Square	0.844
Adjusted R Square	0.819
Standard Error	0.122
Observations	37

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	2.52	0.50	33.65	1.21E-11
Residual	31	0.46	0.01		
Total	36	2.98			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-11.65	2.84	-4.10	2.77E-04	-17.45	-5.85
Ln previous year demand	0.50	0.12	4.21	2.02E-04	0.26	0.74
Ln world GDP (constant 2005US$)	0.51	0.11	4.69	5.27E-05	0.29	0.73
Ln Pt price (constant 1998 US$)	-0.32	0.10	-3.30	2.46E-03	-0.52	-0.12
Ln Ir price (constant 1998 US$)	0.13	0.04	3.22	3.03E-03	0.05	0.20
Ln Mo price (constant 1998 US$)	0.17	0.04	3.86	5.37E-04	0.08	0.26

Table S7 Summary of regression analysis for Pt electrical

Regression Statistics	
Multiple R	0.862
R Square	0.743
Adjusted R Square	0.719
Standard Error	0.147
Observations	37

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	2.06	0.69	31.72	7.73E-10
Residual	33	0.71	0.02		
Total	36	2.77			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	2.05	0.68	3.02	4.81E-03	0.67	3.42
Ln previous year demand	0.73	0.11	6.55	1.91E-07	0.50	0.95
Ln Pt price (constant 1998 US$)	-0.20	0.07	-2.65	0.012	-0.35	-0.05
Ln Pd price (constant 1998 US$)	0.13	0.07	1.88	0.068	-0.01	0.28

Table S8 Summary of regression analysis for Pt glass

Regression Statistics	
Multiple R	0.854
R Square	0.729
Adjusted R Square	0.711
Standard Error	0.267
Observations	33

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	2	5.75	2.88	40.40	3.08E-09
Residual	30	2.14	0.07		
Total	32	7.89			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-12.36	7.36	-1.68	1.03E-01	-27.38	2.67
Ln previous year demand	0.61	0.14	4.35	1.46E-04	0.33	0.90
Ln world GDP (constant 2005US$)	0.46	0.25	1.82	7.86E-02	-0.06	0.98

Table S9 Summary of regression analysis for Pt investment[b]

Regression Statistics	
Multiple R	0.645
R Square	0.416
Adjusted R Square	0.346
Standard Error	0.811
Observations	29

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	11.73	3.91	5.94	3.34E-03
Residual	25	16.46	0.66		
Total	28	28.20			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-48.40	23.32	-2.08	4.84E-02	-96.43	-0.38
Ln world GDP (constant 2005US$)	1.69	0.79	2.14	4.26E-02	0.06	3.32
Ln Pt price (constant 1998 US$)	-2.68	0.88	-3.03	5.58E-03	-4.50	-0.86
Ln Au price (constant 1998 US$)	2.93	0.71	4.12	3.66E-04	1.46	4.39

[b] Investment data are reported as net purchases by the market, and so negative demand values were reported for certain years. Values for the years in which negative net purchases were reported were excluded from the analysis.

Table S10 Summary of regression analysis for Pt jewellery

Regression Statistics	
Multiple R	0.961
R Square	0.923
Adjusted R Square	0.914
Standard Error	0.146
Observations	38

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	8.44	2.11	99.49	6.27E-18
Residual	33	0.70	0.02		
Total	37	9.14			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-33.81	2.49	-13.59	4.51E-15	33.88	-28.75
Ln world GDP (constant 2005US$)	1.44	0.08	17.20	4.82E-18	1.27	1.61
Ln Pt price (constant 1998 US$)	-0.70	0.09	-7.47	1.39E-08	-0.90	-0.51
Ln Pd price (constant 1998 US$)	0.21	0.06	3.35	2.04E-03	0.08	0.34
Ln Ni price (constant 1998 US$)	0.21	0.08	2.76	9.25E-03	0.06	0.37

Table S11 Summary of regression analysis for Pt petroleum

Regression Statistics	
Multiple R	0.909
R Square	0.826
Adjusted R Square	0.803
Standard Error	0.336
Observations	27

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	12.27	4.09	36.28	6.88E-09
Residual	23	2.59	0.11		
Total	26	14.86			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-55.63	12.26	-4.54	1.48E-04	-81.00	-30.26
Ln world GDP (constant 2005US$)	1.28	0.53	2.39	2.56E-02	0.17	2.38
Ln world petroleum refinery output	2.09	0.49	4.27	2.88E-04	1.08	3.10
Ln Pt price (constant 1998 US$)	-0.45	0.22	-2.07	5.03E-02	-0.89	0.00

Table S12 Summary of regression analysis for Pt other applications

Regression Statistics	
Multiple R	0.871
R Square	0.758
Adjusted R Square	0.736
Standard Error	0.207
Observations	37

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	4.44	1.48	34.54	2.72E-10
Residual	33	1.41	0.04		
Total	36	5.85			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	1.30	0.72	1.80	8.15E-02	-0.17	2.78
Ln previous year demand	0.72	0.10	7.47	1.37E-08	0.53	0.92
Ln Pt price (constant 1998 US$)	-0.19	0.10	-1.91	6.45E-02	-0.40	0.01
Ln Pd price (constant 1998 US$)	0.27	0.09	3.04	4.65E-03	0.09	0.45

Table S13 Summary of regression analysis for Pt overall

Regression Statistics	
Multiple R	0.990
R Square	0.981
Adjusted R Square	0.979
Standard Error	0.067
Observations	37

ANOVA

	Df	*SS*	*MS*	*F*	*Significance F*
Regression	3	7.53	2.51	561.01	2.25E-28
Residual	33	0.15	0.00		
Total	36	7.68			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-13.12	3.73	-3.52	1.29E-03	-20.71	-5.54
Ln previous year demand	0.66	0.10	6.67	1.37E-07	0.46	0.86
Ln world GDP (constant 2005US$)	0.54	0.15	3.66	8.82E-04	0.24	0.84
Ln Pt price (constant 1998 US$)	-0.10	0.03	-3.32	2.20E-03	-0.17	-0.04

Table S14 Summary of regression analysis for Pd autocatalyst

Regression Statistics	
Multiple R	0.992
R Square	0.983
Adjusted R Square	0.981
Standard Error	0.178
Observations	32

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	51.00	12.75	400.23	1.32E-23
Residual	27	0.86	0.03		
Total	31	51.86			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-36.13	11.02	-3.28	2.87E-03	-58.73	-13.52
Ln previous year demand	0.76	0.08	10.05	1.29E-10	0.60	0.91
Ln world GDP (constant 2005US$)	1.30	0.38	3.39	2.14E-03	0.51	2.09
Ln Pt price (constant 1998 US$)	-0.29	0.11	-2.66	1.31E-02	-0.51	-0.07
Ln Rh price (constant 1998 US$)	-011	0.05	-2.17	3.87E-02	-0.22	-0.01

Table S15 Summary of regression analysis for Pd chemical

Regression Statistics	
Multiple R	0.953
R Square	0.909
Adjusted R Square	0.901
Standard Error	0.104
Observations	27

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	2	2.58	1.29	119.83	3.24E-13
Residual	24	0.26	0.01		
Total	26	2.84			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-34.47	3.17	-10.87	9.44E-11	-41.02	-27.92
Ln world GDP (constant 2005US$)	1.28	0.10	12.76	3.45E-12	1.08	1.49
Ln Ni price (constant 1998 US$)	0.11	0.05	2.37	2.61E-02	0.01	0.21

Table S16 Summary of regression analysis for Pd dental

Regression Statistics	
Multiple R	0.963
R Square	0.927
Adjusted R Square	0.919
Standard Error	0.086
Observations	32

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	3	2.61	0.87	118.32	5.22E-16
Residual	28	0.21	0.01		
Total	31	2.81			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	2.04	0.45	4.53	9.95E-05	1.12	2.96
Ln previous year demand	0.81	0.06	13.93	4.07E-14	0.69	0.93
Ln Pd price (constant 1998 US$)	-0.16	0.03	-4.77	5.23E-05	-0.23	-0.09
Ln Ni price (constant 1998 US$)	-0.08	0.04	-2.12	4.25E-02	-0.16	0.00

Table S17 Summary of regression analysis for Pd electrical

Regression Statistics	
Multiple R	0.805
R Square	0.649
Adjusted R Square	0.625
Standard Error	0.220
Observations	32

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	2	2.59	1.30	26.78	2.58E-07
Residual	29	1.40	0.05		
Total	31	4.00			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	2.99	0.82	3.65	1.01E-03	1.32	4.67
Ln previous year demand	0.73	0.10	7.17	6.80E-08	0.52	0.94
Ln Pd price (constant 1998 US$)	-0.19	0.08	-2.27	3.11E-02	-0.36	-0.02

Table S18 Summary of regression analysis for Pd investment

Regression Statistics	
Multiple R	0.867
R Square	0.752
Adjusted R Square	0.712
Standard Error	0.932
Observations	30

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	4	65.71	16.43	18.93	2.83E-07
Residual	25	21.70	0.87		
Total	29	87.41			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-57.58	24.11	-2.39	2.48E-02	-107.22	-7.93
Ln previous year demand	0.49	0.12	4.12	3.66E-04	0.25	0.74
Ln world GDP (constant 2005US$)	1.93	0.78	2.47	2.06E-02	0.32	3.54
Ln Pd price (constant 1998 US$)	-1.84	0.46	-4.01	4.86E-04	-2.79	-0.90
Ln Au price (constant 1998 US$)	1.58	0.58	2.71	1.20E-02	0.38	2.78

Table S19 Summary of regression analysis for Pd jewellery

Regression Statistics	
Multiple R	0.830
R Square	0.689
Adjusted R Square	0.620
Standard Error	0.383
Observations	12

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	2	2.93	1.46	9.98	5.20E-3
Residual	9	1.32	0.15		
Total	11	4.25			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	10.83	1.59	6.82	7.76E-05	7.23	14.42
Ln Pd price (constant 1998 US$)	-0.63	0.28	-2.25	5.08E-02	-1.26	0.00
Ln Ni price (constant 1998 US$)	0.89	0.24	3.65	5.31E-03	0.34	1.44

Table S20 Summary of regression analysis for Pd other applications

Regression Statistics	
Multiple R	0.929
R Square	0.862
Adjusted R Square	0.837
Standard Error	0.240
Observations	33

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	9.73	1.95	33.85	8.13E-11
Residual	27	1.55	0.06		
Total	32	11.28			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	42.03	5.50	7.65	3.18E-08	30.75	53.30
Ln world GDP (constant 2005US$)	-1.03	0.18	-5.65	5.40E-06	-1.40	-0.66
Ln Pt price (constant 1998 US$)	-0.63	0.23	-2.79	9.56E-03	-1.10	-0.17
Ln Rh price (constant 1998 US$)	-0.34	0.06	-5.60	6.11E-06	-0.47	-0.22
Ln Ir price (constant 1998 US$)	0.35	0.07	4.92	3.73E-05	0.20	0.49
Ln Mo price (constant 1998 US$)	0.68	0.10	6.88	2.16E-07	0.48	0.88

Table S21 Summary of regression analysis for Pd overall

Regression Statistics	
Multiple R	0.957
R Square	0.915
Adjusted R Square	0.910
Standard Error	0.153
Observations	33

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	2	7.61	3.81	162.02	8.34E-17
Residual	30	0.70	0.02		
Total	32	8.32			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	-46.60	3.07	-15.19	1.25E-15	-52.87	-40.34
Ln world GDP (constant 2005US$)	1.83	0.10	17.92	1.42E-17	1.62	2.04
Ln Pt price (constant 1998 US$)	-0.30	0.07	-4.07	3.15E-04	-0.45	-0.15

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