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Platinum Group Metal Perovskite Catalysts

PREPARATION AND APPLICATIONS

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Perovskites are a large class of minerals, both naturally occurring and synthetically produced, with important technological applications. In this article, platinum group metal (pgm) perovskites are introduced as a relatively new catalyst material. Due to their high activity, versatile and stable structure and low pgm content, they can offer advantages over conventional catalysts. Some of the typical applications and preparation methods of pgm perovskites are reviewed, with particular focus on their potential use to address current challenges concerning autocatalysts, and in organic chemistry.

The role of the support in heterogeneous pgm catalysis is frequently crucial. The choice of support (usually from carbons, silicas, aluminas, zeolites or other inorganic compounds) can influence the selectivity, activity and longevity of the catalyst. Though catalysts of exceedingly high efficiency are regularly produced, the long-term stability of the pgm system, especially under harsh conditions, can be a problem. In addition, rising pgm demand and costs are incentives towards achieving lower metal loadings and higher activity. Some of these issues can be addressed using pgm-containing perovskites.

The perovskite structure is a highly versatile and widespread mineral form, of great importance in nature and technology (1). They were first described and named by the Russian mineralogist Count Lev Aleksevich von Perovski, who discovered the naturally occurring mineral calcium titanate ($CaTiO_3$). The common feature of perovskites is the generic structure ABO_3, with A and B drawn from a range of metals, subject to certain size constraints. The range of possible cation substitutions is limited by constraints on thermodynamic stability, as represented in terms of the Goldschmidt factor (1). The ideal perovskite has a cubic structure, with an octahedral configuration of the oxygen atoms at each corner around the B atom (Figure 1) (2). The structure can tolerate significant non-stoichiometry and partial substitution. By varying the types of atoms at the A and B sites, the resulting structure will deviate from the ideal depending on the constituent properties (for example, ionic radius, valence and electronegativity). Fractional incorporation of several different elements at specific sites can be achieved through careful design. With non-stoichiometric substitutions, oxygen ion conductivity may be induced by oxygen vacancies (3). Control of substitution in the perovskite matrix is important for tuning the properties of the material. For instance, catalytic activity is apparently determined primarily by the species at the B site (4).

This review focuses on methods of preparation of pgm-substituted perovskites, on their performance as catalysts, and on their principal current and potential uses. As opposed to perovskites used as a support for a metal catalyst, the main consideration here is of perovskites containing the pgm within the mineral lattice; the latter require initial synthesis.

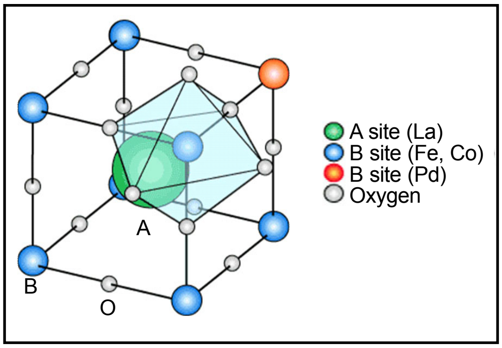


Fig. 1 The perovskite structure (2)

Preparation of PGM Perovskites

Synthetic perovskites may be prepared by a range of methods. Routes similar to those for the production of other ceramics include oxide sintering, combustion synthesis and sol-gel methods (5). Oxide sintering entails heating the powders of the constituents together at high temperature. A variant of this is combustion synthesis, where the ignition of a combustible component provides the energy for the formation of the perovskite mineral. Aqueous combustion synthesis has been used to prepare platinum- and ruthenium-containing perovskites, which were subsequently investigated as anode catalysts in direct methanol fuel cells (DMFCs) (6), a promising technology for portable power applications. Perovskite oxides could provide an alternative to more expensive platinum-based catalysts and a solution to problems of CO poisoning. It was found that $SrRuO_3$ doped with platinum added at the combustion synthesis stage gave performance comparable to that of standard platinum-ruthenium catalysts.

A versatile synthesis of perovskites is by coprecipitation from soluble precursors of the constituent metals in a suitable solvent, followed by solvent removal and heat treatment. S. Petrovic *et al.* prepared palladium-containing perovskites of the form $LaTi_{0.5}Mg_{0.5-x}Pd_xO_3$ ($0 < x < 0.1$) by annealing ethanol solutions of the precursors in a nitrogen flow at 1200°C (7). It was found that at least a proportion of the palladium was not incorporated into the perovskite structure, but existed as a separate metallic phase, which was believed to influence the catalytic activity. The samples were tested in the catalytic combustion of methane, with perovskites with lower palladium loading ($x = 0.05$) showing higher activity at temperatures over 500°C, attributed to the finer dispersion of the palladium in the lattice. Other pgm-containing perovskites have been tested for the combustion of light hydrocarbons, which finds important application in volatile organic compound abatement. Perovskites have been suggested as good candidate catalysts (8), for example lanthanum/cobalt perovskites $La_{1-x}M_xCoO_3$ (M = Ag, Pd, Pt; $0.08 \leq x \leq 0.2$) for catalytic methane combustion (9).

Use of PGM Perovskites in Autocatalysts

Reflecting the trend in pgm usage as a whole (10), the major current use of pgm perovskites is in catalytic converters for cars. Catalytic converters have been in use since the 1970s (11) and usually consist of supports of high surface area, coated with pgms. These systems have proved very successful at simultaneously converting CO into CO_2, unreacted hydrocarbons (HCs) into CO_2 and water and reducing nitrogen oxides (NOx) to nitrogen but, at present, the automotive industry faces several challenges.

The conventional means to meet tightening legislative emissions control targets is simply to increase the amount of pgm in the autocatalyst. The need to guarantee catalyst performance over the typical vehicle lifetime of 80,000 km also means that excess metal must be added, since the performance of the catalyst drops off over time. In the harsh conditions experienced in the exhaust stream with temperatures up to 1000°C, the metal in the catalyst is prone to deactivation by sintering, leading to a reduction in surface area and hence catalytic activity. This issue of ageing performance is expected to become even more important, as the Euro 5 requirements (12) also include an extension of catalyst lifetime to 160,000 km. The robustness of perovskites and the low pgm content typical in pgm-doped perovskites combine to provide a novel solution to these problems.

The palladium-containing perovskite $LaFe_{0.77}Co_{0.17}Pd_{0.06}O_3$, synthesised by coprecipitation of the metal nitrates and perovskite-supported palladium ($LaFe_{0.8}Co_{0.2}O_3$/Pd at the same palladium loading), were compared for their preparation methods and catalytic behaviour by K. Zhou *et al.* (13). Both showed excellent three-way catalytic activity, with the supported palladium somewhat better; this is attributed to greater ease of reduction of the surface palladium to generate the active catalyst compared to the palladium in the perovskite, which was shown to be dispersed throughout the lattice by X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies. Platinum-promoted lanthanum manganate type perovskite catalysts, prepared by coprecipitation of the metal hydroxides using aqueous ammonia, have also shown potential for automobile applications (14), and ruthenium perovskites $La_ySr_{1-y}Ru_xCr_{1-x}O_3$ ($y = 0.7$; $0.025 \leq x \leq 0.100$) have been tested as candidates for lean NOx automotive emission control (15).

Work by H. Tanaka and coworkers at Daihatsu Motors has produced a range of palladium perovskites from soluble alkoxide precursors (16). The salts of the constituent metals were combined in toluene in the desired proportions. Hydrolysis of the salts with water gave a precipitate which was isolated and dried in air to obtain the perovskites. For example, palladium-containing perovskite $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ was prepared from lanthanum, cobalt and iron ethoxyethylates with aqueous palladium nitrate solution (16), and $LaFe_{0.95}Pd_{0.05}O_3$ was synthesised from base metal ethoxyethylates and palladium acetylacetonate (17). Recently, using the same method, platinum- and rhodium-containing perovskites $CaTi_{0.95}Pt_{0.05}O_3$ and $LaFe_{0.95}Rh_{0.05}O_3$ respectively, were also prepared (18, 19).

The use of these perovskites in autocatalysts centres around a novel mechanism which exploits the inherent fluctuations between reducing and oxidising atmospheres in the exhaust gases. In a modern three-way catalytic converter, the exhaust stream over the catalyst is controlled to give optimal conditions for the required reactions. This is achieved by control of the air-to-fuel ratio in the engine, using an oxygen sensor which continually monitors the exhaust gas composition and feeds information back to the air intakes. Inevitable time lags between sensing and adjustment lead to alternations between conditions which are oxygen rich and oxygen poor relative to the ideal stoichiometry.

As synthesised, and under oxidising exhaust conditions, the palladium in $LaFe_{0.95}Pd_{0.05}O_3$ exists as a solid solution dispersed throughout the perovskite lattice. However, under reducing conditions and the high temperatures in the exhaust stream, the palladium segregates to form metallic nanoparticles (1 to 3 nm in size). This process was shown to be reversible, with the palladium redispersing in the lattice on a return to oxidising conditions (Figure 2) (19). This phenomenon accounts for the excellent ageing performance of the perovskite autocatalysts. In conventional autocatalysts using pgm dispersed on a support, sintering over time to ever larger metal particles at the prevailing elevated temperatures leads to a reduction in catalytic activity. In the perovskite catalyst, the oxidising/reducing cycle maintains the catalytic activity by regenerating the palladium metal nanoparticles and preventing metal particle growth. This has led to the catalysts being dubbed 'intelligent', due to their capacity to react to their environment, resulting in greater efficiency (16). Recently, the same effect has been shown in platinum and rhodium perovskites, extending the concept to the full range of pgms commonly used

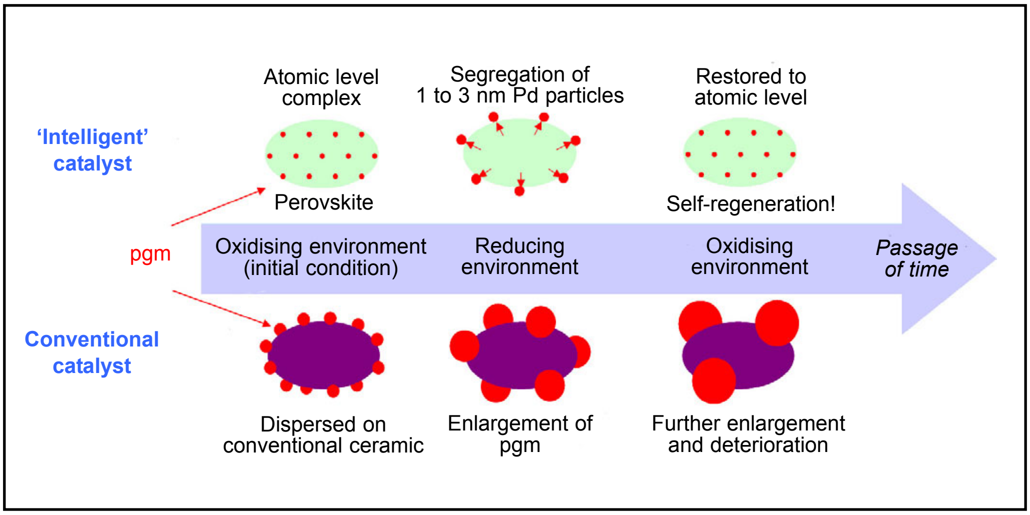


Fig. 2 Schematic of the operation of self-regenerating pgm perovskite autocatalysts (2)

in autocatalysts (18, 19).

The perovskite-containing catalytic converters are also highly active. A vehicle equipped with such a high activity perovskite autocatalyst achieved the J-ULEV (Japan Ultra Low Emissions Vehicle) emissions standard in 2002, demonstrating that pollutant levels more than 50% below those required by current legislation were measured. Another major advantage of perovskite autocatalysts is the reduced metal content compared with that of conventional autocatalysts of similar activity. Reductions of 70 to 90% have been reported possible (20), translating into potentially significant cost savings.

PGM Perovskites in Organic Synthesis

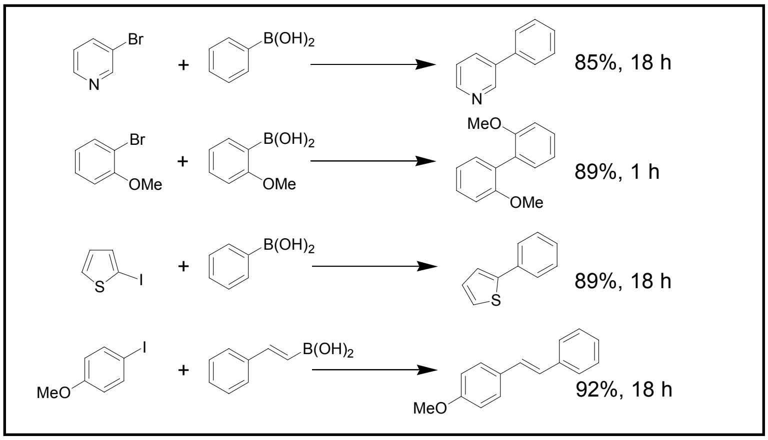
Reactions catalysed by pgms, such as cross-couplings and hydrogenations, are becoming increasingly prevalent in organic synthesis. Where the pgm-catalysed steps are part of the synthesis of active pharmaceutical intermediates (APIs), there are stringent limits on permissible metal contamination, driving a requirement to minimise the release of metals into the process (21). Conventional approaches to achieve this are to move from homogeneous to heterogeneous catalysts, or to 'heterogenise' catalysts *via* processes such as immobilisation (22) or microencapsulation (23).

This is another area where the stability, robustness and low pgm content of perovskite catalysts facilitate their application. The perovskite minerals which are air-stable powders are well suited to use in the chemical laboratory. Professor Steven Ley and coworkers at the University of Cambridge, U.K., have tested palladium-containing perovskites in organic transformations which are otherwise carried out with conventional palladium catalysts (24).

Use of perovskite catalysts in a standard Suzuki coupling, between an aryl bromide and aryl boronic acid, showed that the reaction was catalysed with similar rates by a wide range of perovskites containing 5 at.% palladium (25). It also demonstrated that palladium was an essential component for successful conversion, and that the oxidised form of the perovskites worked better under the reaction conditions. Working with the best-performing catalyst, $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$, M. D. Smith *et al.* extended the perovskite-catalysed Suzuki reaction to encompass a wide range of different substrates, including aryl iodides and bromides, heteroaryl halides and aryl and alkenyl boronic acids (Scheme I) (26). The application of microwave heating also enabled coupling to aryl chlorides.

The use of a copper-palladium perovskite $LaFe_{0.57}Cu_{0.38}Pd_{0.05}O_3$ allowed the extension of perovskite-catalysed organic chemistry to the Sonogashira coupling reaction of aryl halides and acetylenes (27), again giving good yield across a range of aryl bromide and iodides.

There has been considerable work on ascertaining the mechanism by which perovskites function in organic reactions. The lower temperatures involved (typically 80°C) preclude the type of self-regeneration seen in autocatalysts. Investigation focused on whether the reaction proceeded *via* a homogeneous or heterogeneous mechanism, and evidence has



Scheme I A selection of reactions catalysed by palladium perovskite (Conditions: $LaFe_{0.57}Co_{0.38}Pd_{0.05}O_3$ (0.05 mol% Pd), 3 eq. K_2CO_3, 1.5 eq. boronic acid, 1:1 IPA:H_2O, 80°C) (26) been built up by several methods (25). Removal of the bulk catalyst by filtration at partial reaction, followed by returning the filtrate to the reaction conditions, showed that the reaction progressed to significantly higher conversions in the absence of the solid catalyst. This demonstrated that an active solution palladium species was formed, a conclusion supported by solution and solid-phase catalyst poisoning studies. Performance in a three-phase test, employing solution and solid-supported substrates, provides further evidence to support the hypothesis of an active solution species, but also demonstrated that an aryl halide must be present in the solution phase for the reaction to proceed.

Collation of the evidence (25) led to the proposed mechanism shown in Figure 3. The initial step is a reduction of the Pd(III) or other high-valent palladium species in the perovskite, possibly by the solvent, to form a surface-bound Pd(0) species. This is next taken into solution by oxidative addition to the aryl halide. The coupling reaction can now proceed through a fairly conventional solution catalytic cycle, at the end of which the palladium either remains in solution to continue the reaction or is readsorbed onto the perovskite surface.

The release of highly active palladium into solution from the perovskite explains a very efficient catalytic turnover, with loadings of less than 0.05 mol% palladium sufficient. Recapture of the palladium by the perovskite at the end of the reaction cycle accounts for the extremely low residual palladium levels found in the crude reaction products. Palladium contents of less than 2 ppm were found in a Suzuki coupling product (26). The combined benefits of a highly efficient catalyst with low pgm content and very low levels of metal contamination make these attractive catalysts for chemical applications, especially synthesis of pharmaceutical and electronic materials, where exclusion of catalyst residues is essential. Furthermore, the perovskite catalysts have been shown to be recyclable (26), leading to even greater potential cost savings over catalysts which must be disposed of after a single use.

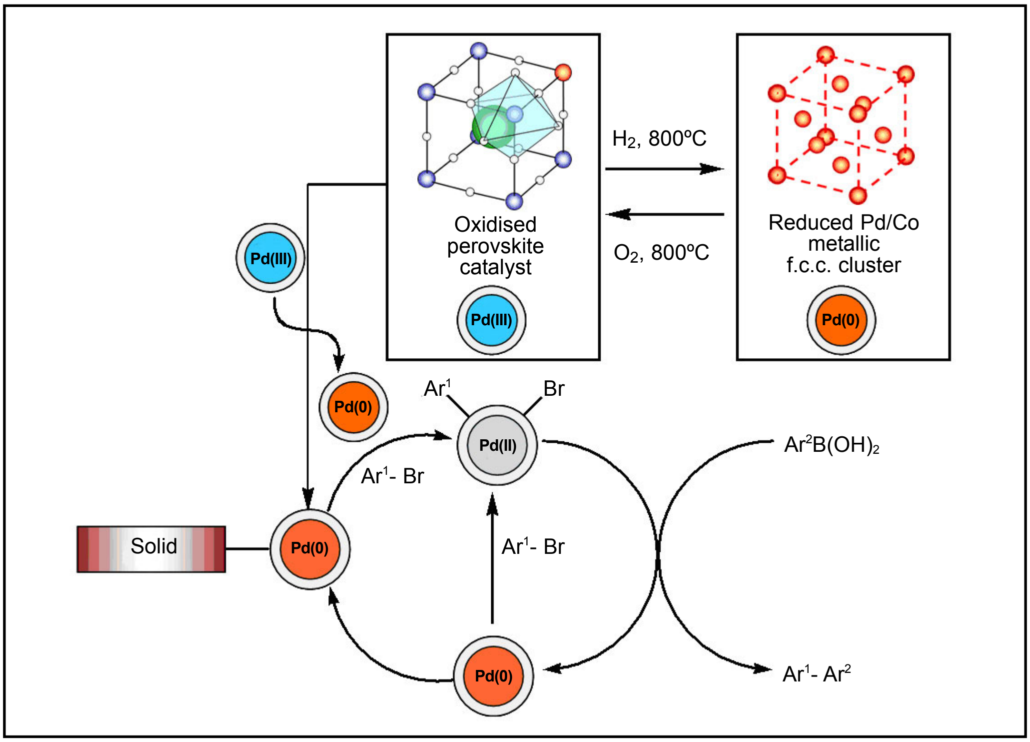


Fig. 3 Proposed mechanism for catalytic activity of pgm perovskites in organic synthesis (25)

Conclusions

The pgm-containing perovskites constitute an active and expanding area of research. The potential and versatility of pgm-containing perovskites as catalysts is shown by the range of applications in which they have been tested – from catalytic combustion to organic synthesis. Their sturdy mineral structure and stability offer advantages wherever high temperatures are involved and in some cases, such as self-regenerating autocatalysts, give distinct benefits where other metal supports are deactivated over time. The high activity often associated with pgm perovskites, combined with the low loadings of pgms required, result in their offering significant potential savings in metal costs. In the organic chemistry laboratory, where the stable, easily handled pgm perovskites work as highly active and clean catalysts, a whole new application area may open in the near future, reinforcing their significance.

The Author

Thomas Screen was born in London, U.K. He studied Natural Sciences (Chemistry) at the University of Cambridge, U.K., where he was awarded a B.A. in 1996. This was followed by two years working at Johnson Matthey Catalytic Systems Division in Royston before returning to academia and the group of Professor Harry L. Anderson at the University of Oxford. Thomas completed his D.Phil. there on the 'Synthesis and Properties of Conjugated Porphyrin Polymers' in 2002 before moving to Germany for a postdoctoral appointment with Professor Klaus Müllen at the Max Planck Institute for Polymer Research in Mainz. On returning to the U.K., Thomas joined Peakdale Molecular Ltd in Chapel-en-le-Frith, Derbyshire, at the end of 2003. Since 2005 he has worked at the new catalyst technologies company Reaxa Ltd in Manchester, U.K.

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