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Research Paper

Self Regenerating Catalysts : Platinum Group Metal Perovskite Catalysts

Engineering

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ABSTRACT

Until the advent of self- regenerating catalysts, catalytic deactivation proved to be detrimental in the progress of innumerable reactions. Various potentially profitable industries were not considered to be feasible because catalytic deactivation hindered the formation of the industrial products. Catalyst deactivation would require a need of greater catalyst metal, most of them being costly had financial ill effects on the industries. Therefore there was a need for such catalysts which would not deactivate with time and thus would continue to have the same activity throughout the reaction. This need was eventually satiated with the invention of self-regenerating catalysts. These type of catalysts adapt to various external conditions without a decrease in their catalytic activity. The Platinum Group Metal – Perovskite Catalyst is one such self- regenerating catalyst. By its self- regenerating mechanism, it has successfully ameliorated automobile industrial reactions and also many other organic reactions. The PGM- Perovskite Catalyst operates at very high temperatures (at which conventional catalyst start deactivating) without undergoing any deactivation from sintering, aging and coking. Moreover due to their high activity, versatile and stable structure and low PGM content required, they offer greater advantages over the conventional catalysts. Hence knowledge of such catalysts would give rise to greater developments in the future and thus alleviate many of our problems. Some of the typical applications of these catalysts in the automobile industries and organic chemistry, their working mechanism, structure and preparation are reviewed in this article.

Historical Background:

Need and greed are the only driving forces for invention to happen. Any scientific innovation which takes place is because of the need for development or because of the greed for acquiring more luxuries. In the same way, the need for 'something' must have given rise to the discovery of self-regenerating catalysts. This 'something' was mainly related to the automobile industry.

Before the advent of self-regenerating catalysts, control of pollutants in automobile exhausts posed a major problem. Although catalytic convertors were in use, assailants were of the view that the catalytic convertors, which used noble metals, demanded for an increase in the cost of the pollutant removal process. This is because; the catalytic activity was reduced by deactivation of the catalysts and hence more catalyst (more amounts of noble metals) was required which subsequently increased the cost. The deactivation of the catalyst is shown in fig 1. Beset by such a precarious situation, there arose a need for some catalyst which would continue to remain active throughout the process and evade the catalytic deactivation problems. Also such catalyst was needed to operate at a very high temperature of exhaust gas. Furthermore, the catalyst also had to be resistant to lead poisoning and be operational in both oxidative and reductive conditions. Fortunately, with the advent of perovskite catalysts, all these requirements were successfully met.

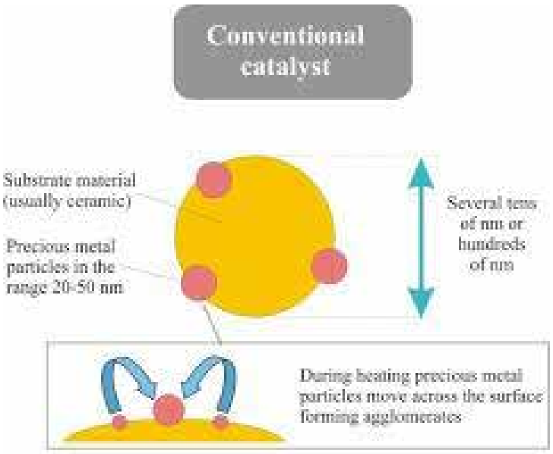


Fig1: Catalytic activity gets reduces due to agglomeration of precious metals[25].

The Platinum Group Metal Perovskite Catalyst (PGM-Perovskite catalyst) is a self-regenerating catalyst. This catalyst has been successfully implemented for use in the emission control process in automobile industry. Moreover this catalyst has also come handy in catalyzing many organic reactions by its self-regenerating mechanism[15],[16],[17],[18],[19]. With these and many more probable applications to unfold in the future, these special or "intelligent" (as they are usually referred to) catalysts would prove to be an elixir for the chemical industry.

Introduction to PGM-Perovskite catalysts:

Perovskites are a large class of minerals, both naturally occurring and synthetically produced, with important technological applications. PGM-Perovskite catalysts, due to their high activity, versatile and stable structure and low pgm content can offer advantageous over conventional catalysts. When used in automotive applications, PGM-Perovskite catalysts catalyze the pollutant control process in a heterogeneous catalysis. While, when used as catalysts in organic synthesis, the same catalyst catalyzes the reaction in a homogenous phase catalysis reaction process. This elucidates on the versatility of these catalysts. As they are regenerating they firstly maintain their catalytic activity throughout the reaction. Secondly, they also require less amount of the precious noble metal due their regenerating mechanism. This reduces the cost of the process. The supports used in heterogeneous pgm catalysis are usually carbons, silicas, aluminas, zeolites or other inorganic compounds.

Chemistry of PGM-Perovskite Catalysts:

PGM during the reaction can exist in two forms depending on the external environmental conditions. It can both be substituted in the perovskite lattice (and thus become a part of the perovskite lattice structure) or it can also be present on the surface of the perovskite as nanoparticles[4]. This has a pivotal role to play in the regenerating mechanism of the catalyst which is exploited in its applications.

The perovskite structure is highly versatile and sturdy. The common feature of perovskites is the generic structure ABO_3 wherein A and B are metals and O stands for oxygen. The ideal perovskite has a cubic structure, with an octahedral configuration of oxygen atoms at each corner around the B atom.

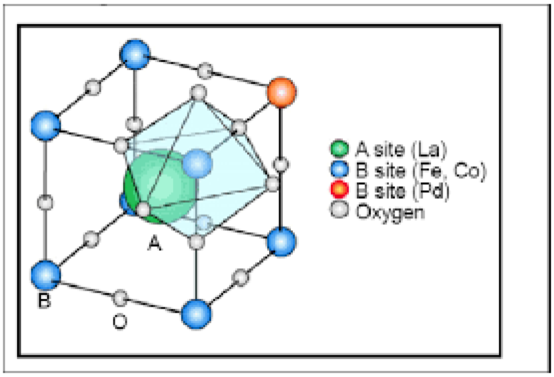


Fig2 Structure of PGM substituted perovskite[4].

This structure is very sturdy and thus can tolerate significant non-stoichiometry and partial substitution[4]. The structure of PGM containing Perovskite is shown in fig2 above.

Preparation of PGM Perovskites:
Synthetic Perovskites may be produced by a range of methods like oxide sintering, combustion synthesis, sol-gel methods etc[5]. But 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 prepared palladium-containing perovskites of the form LaTi0.5Mg (0.5–x) PdxO3 ($0 < x < 0.1$) by annealing ethanol solutions of the precursors in a nitrogen flow at 1200°C[6]. 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.

Application of PGM-Perovskite Catalysts in automobile industry:
The major current use of PGM Perovskite catalysts is in the catalytic converters for cars. The robustness of perovskites and the low pgm content typical in the pgm-doped perovskites combine to provide a novel solution to the problems faced in pollutant emission control in automobiles.

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(Shown in Fig3 and Fig4). 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.

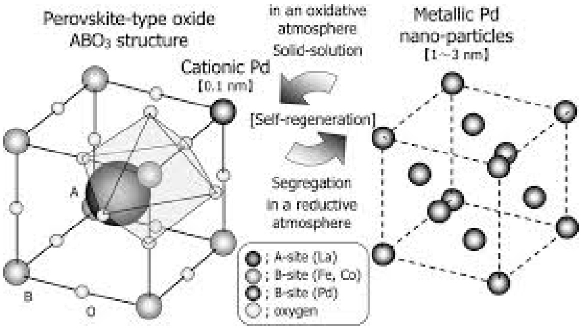


Fig 3 Structure of the catalyst during self regeneration[24].

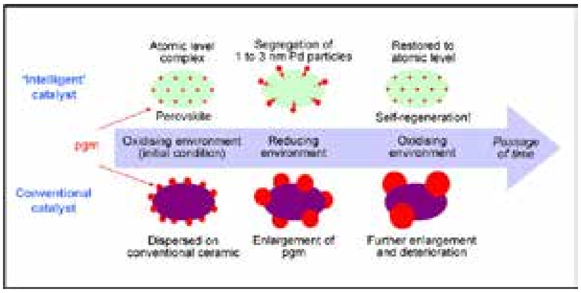


Fig 4: Fluctuations of self regenerating catalyst as opposed to conventional catalyst in different environments[1].

As synthesized, and under oxidizing exhaust conditions, the palladium in LaFe0.95Pd0.05O3 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 oxidizing conditions[13]. 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 oxidizing/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[10](also shown in fig 5). Recently, the same effect has been shown in platinum and rhodium perovskites, extending the concept to the full range of pgms commonly used in autocatalysts[12],[13].

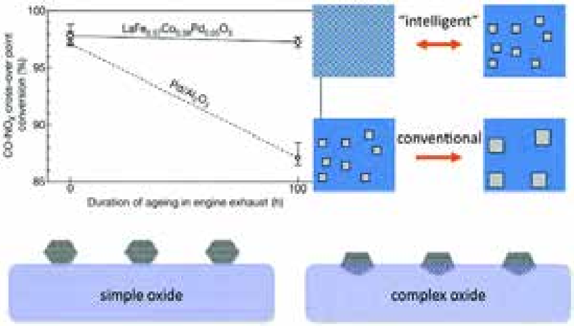


Fig5: A comparison between conventional catalyst and self-regenerating catalyst[3].

Comparison between the precious metals used in perovskite catalysts:

Palladium, Platinum, Rhodium are the precious metals which can be used in these self-regenerating catalysts over the perovskite supports{Shown in fig6(a,b,c) below}.

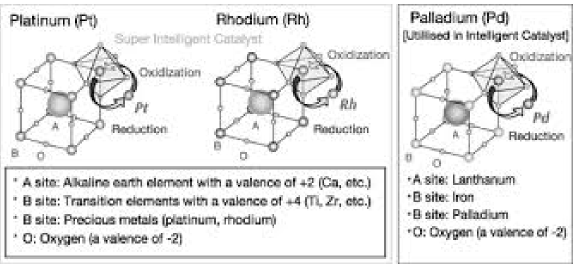
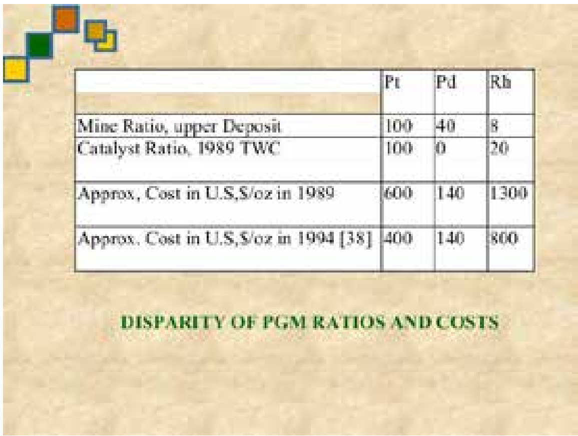


Fig6(a) [24].



	Pt	Pd	Rh
Mine Ratio, upper Deposit	100	40	8
Catalyst Ratio, 1989 TWC	100	0	20
Approx, Cost in U.S,$/oz in 1989	600	140	1300
Approx. Cost in U.S,$/oz in 1994 [38]	400	140	800

DISPARITY OF PGM RATIOS AND COSTS

Fig6(b) [22]

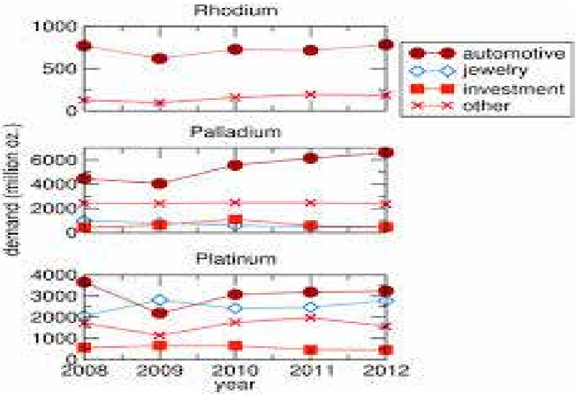


Fig6© [23]

Fig6: Comparison between different Platinum Group Metals with perovskite catalysts.

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[14], translating into potentially significant cost savings.

PGM-Perovskites in Organic synthesis:

Reactions catalyzed 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 minimize the release of metals into the process[15]. Conventional approaches to achieve this are to move from homogeneous to heterogeneous catalysts, or to ‘ heterogenize ’ catalysts via processes such as immobilization[16] or microencapsulation.

This is another area where the stability, robustness and low pgm content of perovskite catalysts facilitate their application.

Mechanism of catalysis of PGM-Perovskite catalysts in organic reactions:

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 been built up by several methods[17]. 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[17] led to the proposed mechanism shown in figure 7 below. 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.

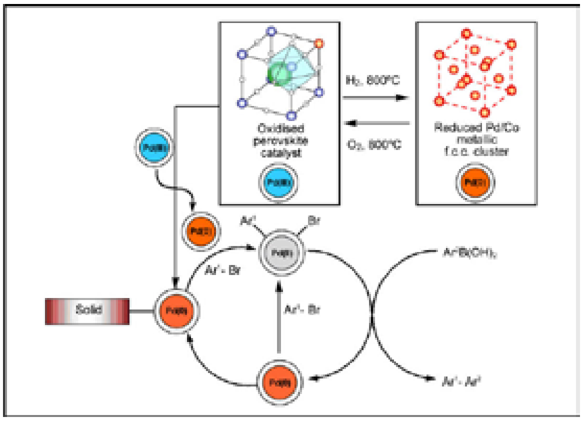


Fig 7: Proposed mechanism for catalytic activity of pgm perovskites in organic synthesis[1].

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[18]. 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[18], leading to even greater potential cost savings over catalysts which must be disposed of after a single use.

Examples of reactions organic reactions catalyzed by PGM-Perovskites:

A selection of reactions catalyzed by palladium perovskite (Conditions: LaFe0.57Co0.38Pd0.05O3 (0.05 mol% Pd), 3 eq. K2CO3, 1.5 eq. boronic acid, 1:1 IPA: H2O, 80°C). Fig8 below shows some reactions that are catalyzed by these catalysts.

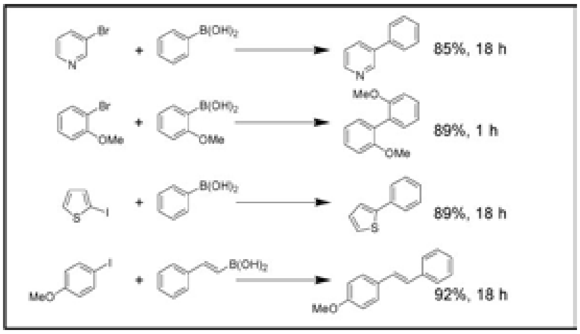


Fig 8: Organic reactions catalyzed by PGM-Perovskite catalysts[1].

The use of a copper-palladium perovskiteLaFe0.57Cu0.38Pd0.05O3 allowed the extension of perovskite-catalyzed organic chemistry to the Sonogashira coupling reaction of aryl halides and acetylenes (19), again giving good yield across a range of aryl bromide and iodides.

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.

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