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Platinum Group Metal Based Nanocatalysts for Environmental Decontamination

Sarve M.K. Nzaba, Bhekie B. Mamba and Alex T. Kuvarega

Abstract

Research and development in chemical engineering is currently focused on design of highly active and selective catalytic systems for process intensification. In recent years, there has been growing interest in the use of catalysts based on nanosized metal particles to improve catalytic processes. Among the many metal catalysts, platinum group metals (PGMs) have received greater attention because of their physical and catalytic properties. They have found applications in a wide range of chemical conversion and environmental decontamination reactions due to their chemical stability and enhanced catalytic reactivity in the nano range. This chapter reviews some of the major innovative applications of PGM nanocatalysts for catalytic environmental decontamination.

Keywords: nanocatalyst, decontamination, platinum group metal, organic transformation, water treatment

1. Introduction

Industrialization and rapid population growth has resulted in energy shortages and environmental contamination which has raised concern of a potential global crisis. For sustainable human society development, technologies for environmental decontamination need urgent attention. Among numerous available technologies, catalysis has gained considerable attention because of the diverse potentials in energy and environmental applications. Generally, catalysts for environmental applications are based on less expensive materials that will not cause secondary environmental pollution [1]. The major advantage of environmental catalysis is the chemical conversion of pollutants into non-hazardous and less toxic products. Pollutants can be degraded and transformed efficiently through homogenous or heterogeneous oxidation and reduction processes under ambient conditions or conditions in which external energy such as light may be required [2]. Therefore, the present book chapter aims to provide analysis in the use of PGMs nanocatalysts in the recent development and appraise their potential applications in environmental decontamination.

1.1 Nanotechnology and the environment

Nanotechnology refers to the research and development of materials at the atomic, molecular or macromolecular scale. Materials at nanoscale find applications in a myriad of areas, such as magnetic and optoelectronic, biomedical, pharmaceutical, cosmetic, energy, electronic, catalytic, and environmental domains. Because of the

potential of nanotechnology, there has been a worldwide increase in investment in nanotechnology research and development [3]. The unique properties of materials and their stupendous performance at nanoscale are the main reason for the increased growth in this area. Controlled assembly of nanoparticles has been proposed as one of the most ways to achieve the target technologies [4]. Nanotechnology has immense potential in environmental decontamination through the use of materials such as adsorbents and nanocatalysts. Therefore, it is necessary to develop novel processes for the fabrication of nanomaterials that can be used as the basis for the development of highly efficient new technologies for solving environment challenges.

1.2 Platinum group metals

Platinum group metals (PGMs) including iridium (Ir), osmium (Os), platinum (Pt), palladium (Pd), rhodium (Rh) and ruthenium (Ru) have high resistance to corrosion and oxidation in moist air, unlike most base metals [5]. Their precious nature derives from their rarity in Earth's crust. It has been reported by Grabowska et al., that PGMs such as platinum and palladium allow the extension of light absorption of semiconductors such as TiO_2 into the visible region [6].

Recently, Dozzi et al. has investigated the catalytic effect of PGMs metal for the degradation of formic acid using Pt, Au doped TiO_2 [7]. On the other hand, Kisch et al. modified TiO_2 with chloride complexes of Pt for the photocatalytic degradation of 4-chlorophenol [8]. The presence of PGMs nanocatalysts gave rise to an enhanced charge carrier separation hence improving the photocatalytic performances of the modified photocatalyst systems. According to Yoon et al., the surface of PGMs serves as visible light absorbing sensitizers and centers of charge separation [9]. The possibility of designing and applying nanosized PGM catalysts has been demonstrated in a number of studies [9–12]. This has resulted in interest in considering their application in environmental remediation, water treatment, chemical transformation and microbial disinfection. A priority task of present day science is to solve the problem of environmental contamination of planetary resources which requires development of efficient technologies employing nanocatalysts. PGMs catalysts have already found applications in a number of industrially important R&D niche areas, including environmental cleanup. The effectiveness of the PGM nanocatalysts depends on a number of factors, including their size, morphology of the particles and their packaging into usable devices and systems. In most of these applications, the cost of PGMs cannot be ignored. Platinum has been reported to be a very good catalyst but a trade-off has to be established between efficacy and cost. In the nano-range the amount of the catalyst is usually kept very low while huge improvements in efficiency are realized. However, there is still need for more effort in design of viable systems for environmental decontamination using PGM based nanocatalysts. Potential up-scaling of these devices and systems is currently an area of increasing research interest.

2. Synthesis of PGM nanocatalysts

Designing a new class of highly selective and active catalytic systems with the use of recent developments in chemistry has become one of the main concerns faced in contemporary engineering. As compared to bulk material, nanoparticles have an increased surface area and high dispersity and, thus provide high reactivity and allow fabrication of efficient catalysts with lower noble metal loading. Controlling the growth, size, and monodispersity of metal nanoparticles is a subject of interest in designing of nanosized catalytic systems. Therefore, different methods have been used for the synthesis of nanocatalysts. For instance, in 2005, Wong et al., successfully

synthesized a bimetallic catalyst using Pd-on-Au NPs through the Turkevich–Frens (citrate reduction) method and obtained particles with an average diameter of about 20 nm [10]. Paula and co-workers synthesized Pd/C-catalyst using one-pot method for synthesis of secondary amines by hydrogenation of nitrocompounds as single starting materials [11]. Additionally, Coleman et al. synthesized and Pt/TiO₂ catalyst by the photodeposition method in the presence of a sacrificial organic hole scavenger [12]. Barakat et al., synthesized Pt doped TiO₂ catalyst by immobilizing colloidal Pt nanoparticles onto titanium dioxide (rutile) [13]. Kuvarega et al., used a modified sol gel method for the synthesis of nitrogen, PGM co doped TiO₂. In these studies spherical particles of average size between 2 and 5 nm were reported [14].

3. Characterization of PGMs based nanocatalysts

Many different physico-chemical techniques are used to characterize nanocatalysts among them scanning electron microscopy (SEM) used for the morphology of the materials. Transmission electron microscopy (TEM) is also used for particles size and morphology. Chun-Hua et al. used TEM to analyze 3% Pt nanoparticles supported on CNT particles is shown in **Figure 1**. In another study, Pt catalyst containing 3% metal

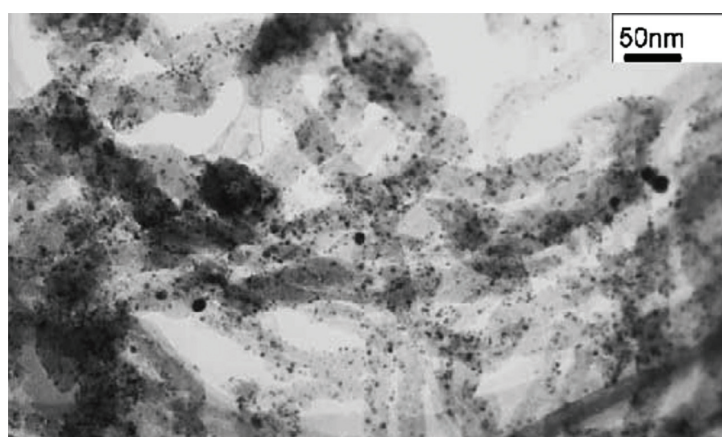


Figure 1. TEM image of 3% Pt/CNT particles (Copyright, J. Mol. Catal. A: Chem., Ref. [17]).

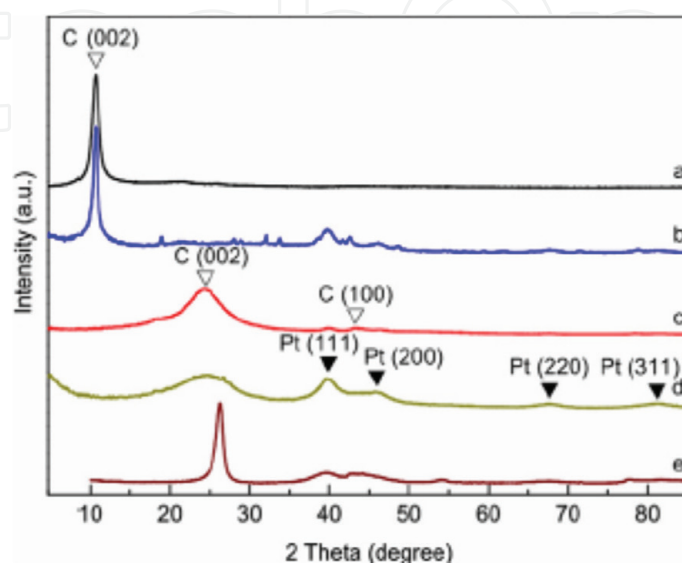


Figure 2. XRD patterns of (a) GO, (b) Pt/RGO-HH, (c) Pt/RGO-EG, (d) Pt/AC-EG and (e) Pt/MWCNT-EG. (Copyright Carbon 50 (2012) 586-596, Ref [18]).

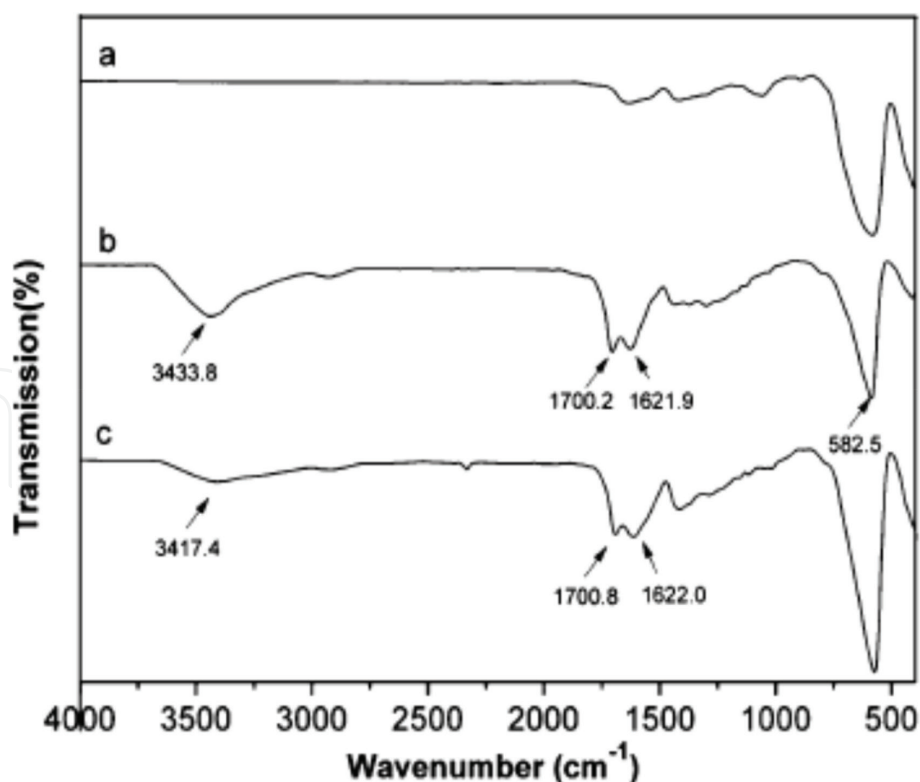


Figure 3. FT-IR spectra of (a) the Fe_3O_4 microspheres, (b) the $\text{Fe}_3\text{O}_4@C$ composite, (c) the $\text{Fe}_3\text{O}_4@C@Pt$ catalyst (reproduced with permission from the Royal Society of Chemistry).

supported on activated carbon (AC) was prepared and the particle size varied from 8 to 10 nm [15]. In addition, techniques such as X-Ray Photoelectron Spectroscopy (XPS) have been used to give information on the oxidation states of the PGM and the nature of bonding between the metals and the supports.

Raman spectroscopy (RS) and X-ray diffraction (XRD) are conducted to identify the crystalline phases and estimate particle sizes of nanocatalysts. For instance, Renfeng et al. used XRD to identify the Pt in Pt/RGO [16]. The Pt peak was conspicuous in the samples containing Pt (**Figure 2**).

Xie and co-workers used Fourier Transform infrared spectroscopy (FTIR) to verify the bond vibrations related to functionalities on the surfaces of their synthesized materials (**Figure 3**) [17].

4. Application of PGMs based nanocatalysts

4.1 Environmental decontamination

PGMs nanocatalysts have become a new class of environmental remediation materials that could provide affordable solutions to some of the environmental challenges. At nanoscale, PGMs particles have high surface areas and surface reactivity. As such, they provide more flexibility for in situ applications. PGMs nanocatalysts have proven to be an excellent choice for the transformation and decontamination of a wide variety of common environmental contaminants, such as organochlorine pesticides and chlorinated organic compounds. The major consumer of PGMs is the automobile industry. PGMs such as Pt, Rh and Pd are used as catalysts in the automobile industry in order to reduce the level of unburnt hydrocarbons, carbon monoxide (CO) and nitrogen oxide present in the exhaust gases. Generally, a typical automobile converter contains 0.04% Pd, 0.005–0.007%

and 0.08% Pt and Rh supported on a base [18]. Iridium has become the new entrant in this application area. A typical example is the introduction of iridium-containing catalytic converters in their direct injection engines by Mitsubishi of Japan [19].

A typical example is the reduction of nitrogen oxides to nitrogen used in car exhaust systems for abatement of emissions from petrol/rich-burn engines. There is a huge number of reports on use of Rhodium as it is the most effective element in the conversion of nitrous oxides to nitrogen [20, 21].

Jianbing et al., in their study, investigated the catalytic ozonation of dimethyl phthalate (DMP) in aqueous solution and DBP precursors in natural water using Ru/AC. These two kinds of organics are both recalcitrant to biodegradation and will cause severe hazards to human health.

Ru/AC was an active nanocatalysts in the catalytic ozonation of dimethyl phthalate and had the ability to complete mineralize the DMP in a semi-batch experiment. On the other hand, the total organic carbon (TOC) removals were stable around 75% for a duration of 42 h and no trace of Ru was observed from the reactor in the continuous experiments of Ru/AC catalyzed ozonation of DMP. Consequently, Ru/AC catalyzed ozonation was found to be more efficient than ozonation alone for TOC removals in the natural water treatment [22].

4.2 Water treatment

Oxyanions, such as BrO_3^- , ClO_3^- , NO_3^- and ClO_4^- are toxic and they are pervasive in drinking water. These oxyanions originate from both anthropogenic and natural sources. Furthermore, they are also produced during water treatment processes such as ozonation, desalination, electrochemical treatment and chlorination [23–26]. These ions have mutagenic, endocrine disrupting and carcinogenic effects [27, 28]. Ion exchange and reverse osmosis cannot completely degrade these oxyanions [28, 29]. Thus, it would be preferable to apply destructive treatment technologies based on nanocatalysts for sustainable drinking water treatment processes [30]. Pd-based heterogeneous catalysis has garnered momentous attention as a potential solution for reduction of these oxyanions and for other highly oxidized contaminants such as halogenated and nitro organics [31]. Chen et al., have used PGMs for the reduction of BrO_3^- [32]. Five activated carbon supported on metal namely (with a 5 wt % Pd, Pt, Rh, Ru and 1 wt% for Ir) with a M/C of 0.1 g L catalysts loading were used for the catalytic reduction of bromated (BrO_3^-) **Figure 4**. From **Figure 4**, it is noticeable that Rh/C was significantly more active than the other PGMs/C catalysts used for the reduction of BrO_3^- .

When catalyst loading 0.1 g L^{-1} was used, a reduction of 1 mM BrO_3^- was achieved in approximately 5 minutes. Rh/C had a much higher activity than most supported metal catalyst reported in literature when compared with metal mass-normalized basis. While each metal catalyst dispersion differs, it was vital to compare the activity of metals hydrogenation using the initial turnover frequency values (TOF_0) [33–35]. Additionally, Rh/C had the best performance compared to the other four catalysts at pH 7.2. On the other hand, Ir/C had a slightly lower apparent reactivity with BrO_3^- than that of Pd/C but was the second highest performance. Therefore, the incorporation of the two PGMs catalysts namely Rh and Ir led to the highest activity for the catalytic reduction of BrO_3^- under condition that are suitable for the water treatment systems.

4.3 Antimicrobial

Microbial contamination and growth on the surfaces are risks to human health. The chemicals used to tackle microbials such as detergents, alcohols and chlorine are very aggressive and hence not environmentally friendly besides being

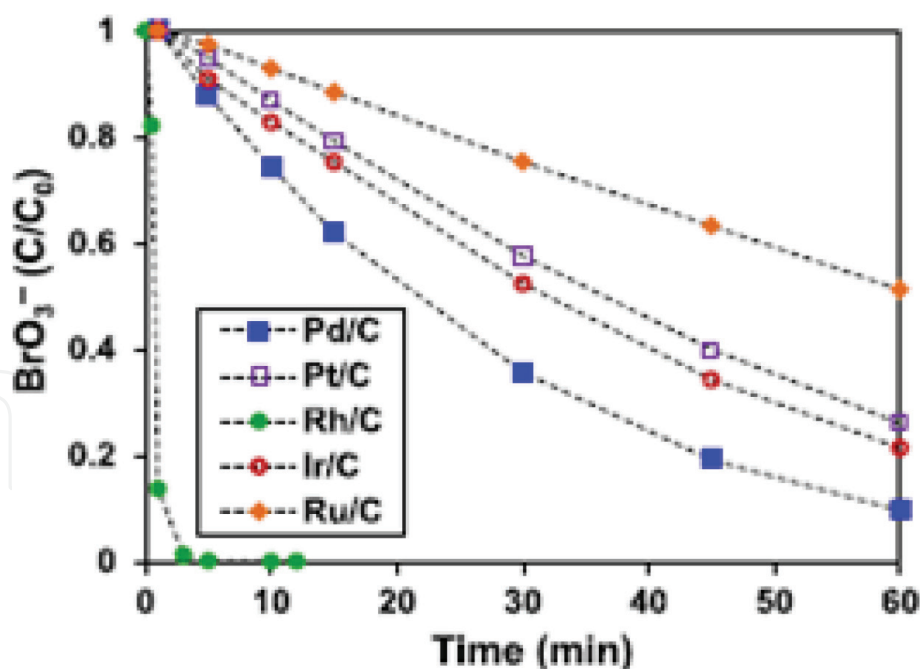


Figure 4. Kinetics of 1 mM BrO_3^- by $0.1 \text{ g L}^{-1} \text{ M/C}$ catalyst at 1 atm H_2 , $\text{pH } 7.2$ and 22°C (with 5 wt\% metal for Pd, Rh, Ru, and Pt; 1 wt\% metal for Ir). (Copyright Chemical Engineering Journal, 313, 2017, 745-752, Ref. [28]).

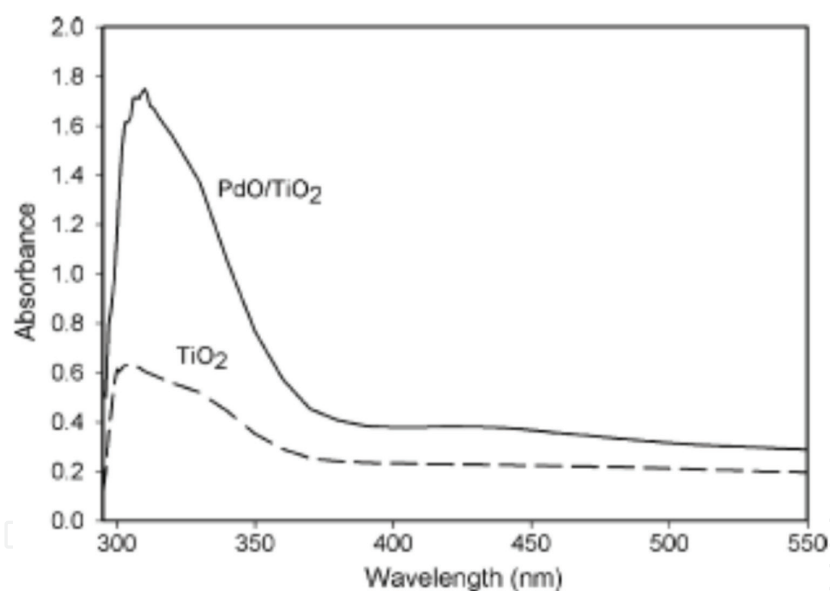


Figure 5. UV-vis spectra of bare TiO_2 and PdO/TiO_2 samples. (Copyright, Chemistry 184 (2006) [34]).

ineffective for long-term disinfection. Therefore, a myriad of studies are being conducted in order to tackle these challenges. Arcan et al. doped SnO_2 and TiO_2 with Pd for microbial inactivation of *E. coli*, *S. aureus* and *S. cerevisiae* [36].

The addition of Pd led to an enhancement in the photocatalytic efficiency observed for the degradation of microorganisms when 1% of Pd was used. In addition, the UV-Vis showed an extension of the absorption edge into the visible range without affecting the phase of the catalysts (Figures 5 and 6).

4.4 Chemical transformation

PGM nanoparticles have proven to be efficient heterogeneous and homogeneous catalysts with advantages such as a high specific surface area due to their small

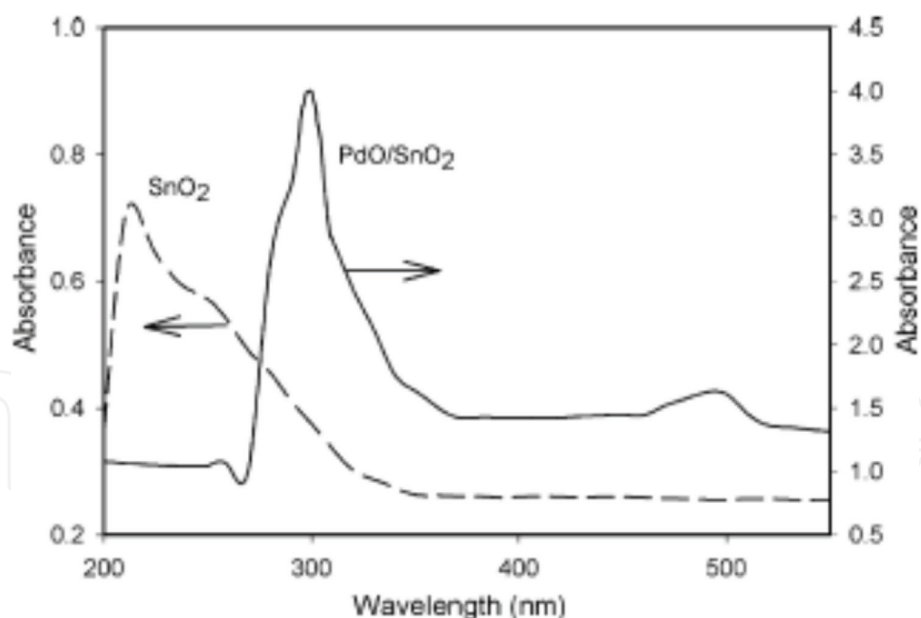


Figure 6.
 UV-vis spectra of bare SnO_2 and PdO/SnO_2 samples. (Copyrights Chemistry 184 (2006) Ref. [34]).

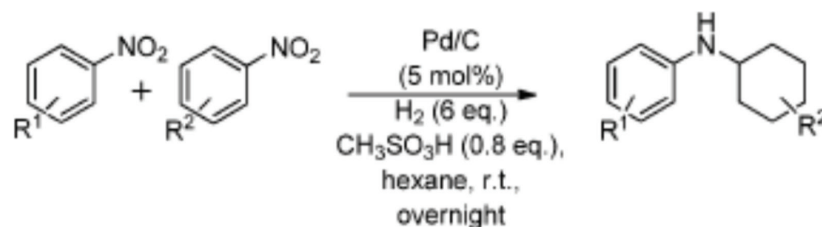


Figure 7.
 Pd/C-catalyzed one-pot synthesis of secondary amines by hydrogenation of nitrocompounds. (Copyright Chem. Commun., 2013, 49, 8160, Ref [10]).

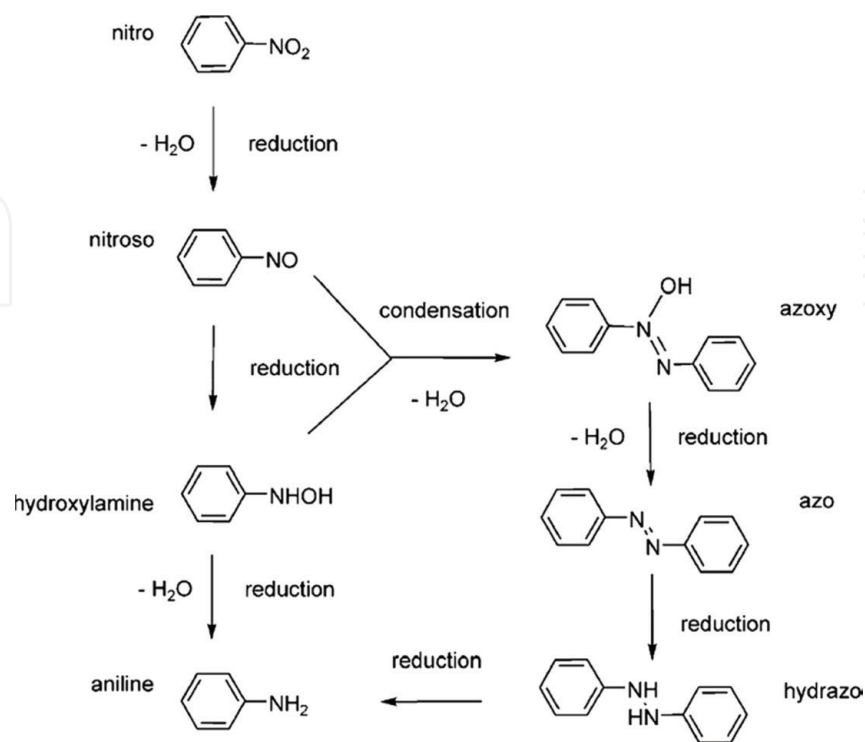


Figure 8.
 Proposed mechanism for the hydrogenation of nitroarenes. (Copyright ChemCatChem, 2009, 1, 210–221, Ref. [38]).

Entry	Substrate	Product	t/min	Conv./%	Sel./%
1 ^a			190	100	92.3
2 ^b			170	100	91.9
3 ^b			115	100	86.3
4 ^b			65	100	86.3
5 ^c			210	100	93.4

Table 1.

Hydrogenations performed using Pt/C as catalysts (*Catal. Sci. Technol.*, 2014, 2445, Ref. [39]).

size resulting in a high number of potential catalytic sites [37]. Owing to these phenomena, there has been in the past two decades an increase in the use of metal nanoparticles in catalysis [38, 39]. Rong et al., reported the synthesis of supported Pt NPs and their use as catalysts in the partial hydrogenation of nitroarenes to arylhydroxylamines [40]. The particles were prepared by reduction of H_2PtCl_6 with NaBH_4 in the presence of the carbon support. The hydrogenation of several substituted nitroarenes was performed under soft conditions (10.15°C , 1 bar H_2) to favor the formation of hydroxylamines, showing excellent activity and selectivity in this transformation. Pd supported on C has also been successfully used as catalysts for the conversion of nitrobenzenes to secondary amines (**Figure 7**).

The proposed mechanism for the hydrogenation of nitrobenzene was proposed as shown in **Figure 8**. During this process, there is generation of intermediates such as hydroxylamines, azo and azoxy derivatives.

For example, in the case of m-dinitrobenzene, a catalyst containing 2 wt% Pt/C yielded 92.3% of the corresponding hydroxylamine after 190 min of reaction in THF (**Table 1**).

In a study, Zeming et al. used carbon as Pt colloid support for the hydrogenation of arylhydroxylamines. The Pt colloid supported on carbon was an active and selective catalyst for the partial hydrogenation of nitroaromatics with electron-withdrawing substituents to the corresponding N-arylhydroxylamine, indicating an additive-free green catalytic approach for arylhydroxylamine synthesis. Very encouraging results were obtained with N-arylhydroxylamine bearing electron-withdrawing substituents. Since N-arylhydroxylamine can be further converted to highly valuable compounds through several reactions like Bamberger rearrangement, this result will generally contribute to a simpler and greener synthetic methodology of N-arylhydroxylamine derivatives.

5. Future perspectives

Progress has been reported in the application of nano-PGMs for heterogeneous catalysis reactions. While most of the applications have centered on organic transformations, there is potential for extending the catalytic potential of these metals to other fields such as pollutant degradation and microbial inactivation in water

treatment processes. On their own, PGM at the nanoscale tend to aggregate and thus limited application has been realized. However, the use of supports has greatly enhanced the activity of the PGM nanocatalysts in various fields. Mono and bimetallic systems have been reported on. In environmental decontamination processes there is still need to find the most suitable supports and application devices. While encouraging findings have started appearing in literature, more work still needs to be done to in environmental catalysis for water treatment.

6. Conclusion

Several efforts have been devoted to the preparation of PGM nanocatalysts for application in environment decontamination. The high number of literature reports highlights the interest in this family of catalysts for catalytic transformation, both in terms of reactivity and selectivity. There is potential for application of PGMs nanocatalysts for environmental decontamination, water treatment, antimicrobial and chemical transformation. Further studies are necessary to better understand parameters influencing the reactivity as well as enhancing the conversion rates and efficiencies.

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Conflict of interest

The authors declare that there is no conflict of interests concerning the publication of this book chapter.

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