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A Review on Preparation of Low Loading Platinum Group Catalyst and Its Application in the Purification of Volatile Organic Compounds (VOCs)

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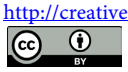

Abstract

Volatile Organic Compounds (VOCs) are harmful air pollutants requiring efficient treatment technologies. Catalytic oxidation using Platinum Group Metal (PGM) catalysts is highly effective but hindered by their high cost. This review explores advanced strategies for fabricating low-loading PGM catalysts to achieve cost-effective VOC purification. The review focuses on synthesis methods such as strong electrostatic adsorption, colloidal synthesis, and single-atom catalyst preparation that maximize atomic efficiency by enhancing metal dispersion and strengthening metal-support interactions. The role of innovative supports, including redox-active oxides, zeolites, and carbon-based materials, in stabilizing low PGM loadings and promoting activity is also discussed. The application of these catalysts in oxidizing VOCs like toluene, formaldehyde, and chlorinated compounds is critically examined, demonstrating that rational design can yield superior performance with minimal metal use, paving the way for sustainable air pollution control.

Subject Areas

Inorganic Chemistry, Inorganic Nonmetallic Materials

Keywords

Platinum Group Metals (PGMs), Low-Loading Catalyst, VOC Oxidation, Metal-Support Interaction, Single-Atom Catalyst, Catalytic Purification, Environmental Catalysis

1. Introduction

Volatile Organic Compounds (VOCs) are a significant class of air pollutants emitted from various industrial processes, vehicle exhaust, and household products, contributing to the formation of ground-level ozone and secondary organic aerosols [1] [2]. Prolonged exposure to VOCs poses serious risks to human health, including carcinogenic and neurological effects [3]. Among the available control technologies, catalytic oxidation is recognized as one of the most efficient and energy-saving methods for VOC elimination, converting these harmful compounds into harmless CO_2 and H_2O at relatively low temperatures [4] [5].

Platinum Group Metal (PGM) catalysts, including Pt, Pd, and Rh, are renowned for their exceptional activity and stability in the complete oxidation of VOCs [6]. However, the high cost and limited global supply of these noble metals present substantial economic barriers to their widespread industrial application [7]. A quantitative comparison underscores this economic advantage. Conventional PGM catalysts for VOC oxidation often employ loadings in the range of 0.5 - 1.5 wt% or higher to achieve a T_{90} (temperature for 90% conversion) of 200˚C - 300˚C for typical VOCs like toluene [6] [7]. In contrast, the advanced low-loading systems discussed in this review (≤0.5 wt%) frequently achieve comparable or even superior T90 values for instance, 190˚C - 240˚C for the same VOC while simultaneously reducing the PGM content by 50% - 90% [8] [9]. This drastic reduction in precious metal use translates to a direct and significant decrease in catalyst cost, as PGMs can constitute the majority of the total expense. Furthermore, strategies like zeolite encapsulation or single-atom anchoring on N-doped carbon can enhance hydrothermal and anti-sintering stability, addressing a key weakness of traditional high-surface-area supported catalysts [9] [10].

Consequently, intensive research efforts have been directed toward developing high-performance catalysts with minimal PGM content. The key challenge lies in maintaining high catalytic activity and stability while significantly reducing the metal loading, which necessitates maximizing the atomic efficiency of the active sites [11]. Here, atomic efficiency refers to the fraction of the total metal atoms that are surface-accessible and actively participate in the catalytic reaction, thereby minimizing the number of inactive atoms buried within nanoparticles.

As a result, research has shifted toward sophisticated catalyst preparation strategies designed to achieve atomic-level metal dispersion, engineer strong metal-support interactions (SMSI), and create tailored support structures [12]. This evolution encompasses catalyst design across multiple scales from single atoms and nanoclusters to nanoparticles each offering distinct advantages for catalytic applications [13]. Techniques such as strong electrostatic adsorption (SEA), deposition-precipitation, and the synthesis of single-atom catalysts (SACs) have emerged as promising avenues for creating highly active sites with ultra-low PGM loadings (<0.5 wt%) [10]. Concurrently, the development of advanced support materials such as mesoporous silica, doped ceria-zirconia, and metal-organic frameworks (MOFs) plays a crucial role in stabilizing these highly dispersed metal

species and facilitating the redox processes essential for VOC oxidation [14] [15].

This review aims to provide a comprehensive overview of the recent advancements in the preparation of low-loading PGM catalysts. It will critically examine the relationship between innovative synthesis methods, the resulting catalyst structure, and the subsequent performance in VOC purification. By comparing different strategies and their outcomes, this review seeks to highlight the most promising pathways for designing cost-effective and high-efficiency catalytic systems for environmental remediation.

2. Overview of Catalyst Preparation Strategies

The performance of low-loading PGM catalysts is intrinsically linked to the preparation method, which dictates critical factors such as metal nanoparticle size, dispersion uniformity, and the nature of metal-support interactions. Conventional techniques like wet impregnation often result in poor metal dispersion and nanoparticle agglomeration at low loadings. This section explores advanced synthesis strategies designed to overcome these limitations and maximize the utilization efficiency of precious metals.

2.1. Impregnation and Adsorption Techniques

Traditional incipient wetness impregnation, while simple, frequently leads to heterogeneous metal distribution. Advanced adsorption techniques have been developed to achieve superior control. Strong Electrostatic Adsorption (SEA) exploits electrostatic interactions between charged metal-complex precursors and an oppositely charged support surface to achieve highly dispersed and stable metal species [16]. By carefully controlling the pH relative to the support's point of zero charge (PZC), a monolayer of metal precursors can be adsorbed, yielding, upon calcination and reduction, nanoparticles with narrow size distributions of 1 - 2 nm even at loadings as low as 0.3 wt% Pt [17].

2.2. Colloidal and Microemulsion Methods

These methods involve the pre-formation of metal nanoparticles with controlled size and shape in a liquid phase, followed by their deposition onto a support. Colloidal synthesis, often using stabilizing agents like polyvinylpyrrolidone (PVP), allows for precise control over nanoparticle size and morphology before deposition [18]. Microemulsion techniques, utilizing water-in-oil emulsions as nanoreactors, can produce uniform nanoparticles with diameters below 3 nm. A key advantage is the decoupling of nanoparticle formation from the support properties, enabling the synthesis of well-defined bimetallic nanoparticles (e.g., Pt-Pd) that can be deposited onto various supports, often resulting in enhanced activity for VOC oxidation compared to monometallic counterparts [19].

2.3. Deposition-Precipitation (DP)

The deposition-precipitation method involves the gradual precipitation of a metal

precursor onto the support surface from a solution, typically by slowly increasing the pH. This technique is highly effective for achieving high metal dispersion, especially on oxide supports like TiO_2 and Al_2O_3 [20]. The slow precipitation kinetics favor the nucleation of metal hydroxides directly on the support surface rather than in the bulk solution, minimizing the formation of large aggregates. This method has been successfully used to prepare catalysts with Pd loadings below 0.5 wt% that exhibit excellent activity for benzene and toluene oxidation [21].

2.4. Single-Atom Catalysts (SACs)

The ultimate expression of maximizing metal utilization is the creation of Single-Atom Catalysts (SACs), in which isolated metal atoms are stabilized on a support. This represents the frontier of low-loading catalyst research [22]. Synthesis of SACs requires meticulous control to prevent atom migration and aggregation. Common strategies include co-precipitation, high-temperature atom trapping, and the use of defect-rich supports where metal atoms can be anchored at vacancies or step edges [23]. For instance, Pt_1/CeO_2 catalysts, with Pt loadings of ~0.1 wt%, have demonstrated exceptional activity for CO and formaldehyde oxidation, as the isolated Pt atoms activate oxygen species on the ceria support with near 100% atomic efficiency [24]. However, challenges remain regarding their stability under harsh reaction conditions and their suitability for reactions requiring ensemble sites.

3. Role of Support Materials

The support is not merely a passive carrier for the active metal but plays an active role in determining the catalytic performance. An optimal support can stabilize highly dispersed metal species, participate in the redox cycle, and influence the adsorption/desorption of reactants and products.

3.1. Metal Oxides

Conventional oxides like γ-Al_2O_3, TiO_2, and SiO_2 are widely used due to their high surface area and stability. However, redox-active oxides such as CeO_2, MnO_2, and Co_3O_4 are particularly advantageous for VOC oxidation [25]. Ceria (CeO_2) and its mixed oxides (e.g., CeO_2-ZrO_2) are prominent for their high oxygen storage capacity (OSC), which facilitates the provision of active oxygen species for oxidation reactions. Strong Metal-Support Interaction (SMSI) in systems like Pt/CeO_2 can lead to the formation of unique interfacial sites with enhanced activity. Doping these oxides with other metals (e.g., Fe, Cu) can further create defects and modulate the electronic properties, improving the dispersion and stability of low-loading PGMs [26].

3.2. Zeolites

Zeolites offer well-defined microporous structures and strong acidity, which can be beneficial for the adsorption and activation of certain VOC molecules. Confin-

ing PGM nanoparticles within zeolite pores (e.g., MFI, FAU) can create size-selective environments and prevent nanoparticle sintering [8]. For example, Pt nanoparticles encapsulated in a Silicalite-1 zeolite exhibited remarkable stability for propane oxidation due to the physical confinement effect. Furthermore, the Brønsted acid sites in zeolites can work synergistically with metal sites, promoting the activation of stubborn VOCs like chlorinated compounds [27].

3.3. Carbon-Based Materials

Activated carbon, carbon nanotubes (CNTs), and graphene derivatives are attractive supports due to their high surface area, tunable surface chemistry, and conductivity. Functionalization of carbon surfaces with oxygen-containing groups (e.g., -COOH, -OH) can provide anchoring sites for PGM precursors, improving dispersion [28]. N-doped carbon materials have shown particular promise, as the nitrogen species can strongly coordinate with single metal atoms, creating highly stable and active M-N_x sites (M = Pt, Pd) analogous to those in metalloenzymes. These catalysts have demonstrated excellent performance for the oxidation of aromatic VOCs [10]. The pivotal roles of different support materials are summarized in **Figure 1**.

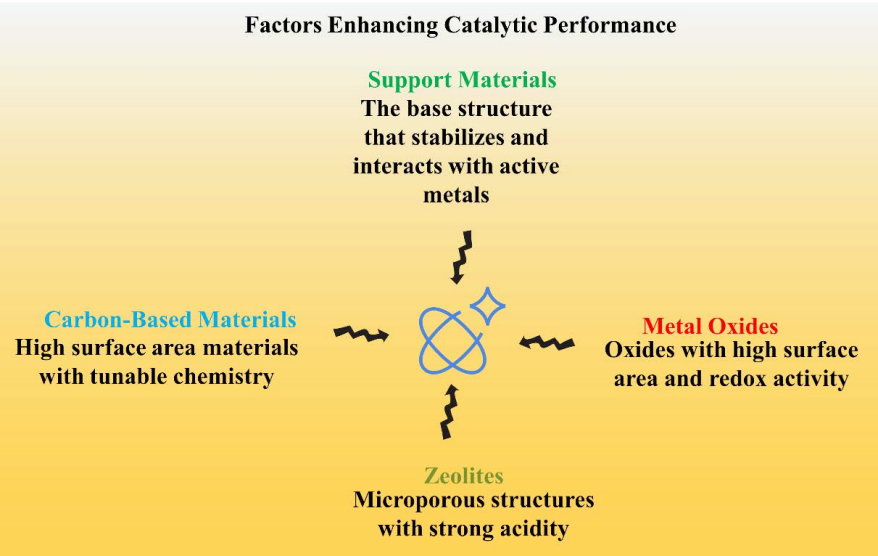

Figure 1. Schematic illustration of the key roles of support materials in low-loading PGM catalysts for VOC oxidation.

4. Deactivation Mechanisms and Mitigation Strategies

The high dispersion and low coordination of active sites in ultra-low PGM catalysts, while beneficial for activity, also increase their susceptibility to specific deactivation pathways. Understanding these mechanisms is essential for designing robust catalytic systems.

Sintering refers to the thermal agglomeration of finely dispersed metal atoms or nanoparticles into larger, less active structures. This is a primary threat during

the high-temperature oxidation of VOCs. The risk is particularly acute in low-loading systems due to the high surface energy of small clusters, which drives Ostwald ripening and particle migration. Mitigation strategies focus on physical confinement and strong anchoring. For example, encapsulating PGM nanoparticles within zeolite pores (e.g., Pt@Silicalite-1) physically restricts their migration [24]. Similarly, using supports with high defect densities or specific anchoring sites such as oxygen vacancies on CeO_2 or nitrogen dopants in carbon matrices can effectively trap single atoms or small clusters, preventing their mobility and coalescence [10] [24].

Chlorine and Sulfur Poisoning from halogenated or sulfur-containing VOCs can cause severe and often irreversible deactivation. Chlorine species form stable surface chlorides that block active sites, while sulfur compounds bind strongly to PGM surfaces. In low-loading catalysts, where the absolute number of active sites is minimal, even minor poisoning can lead to a significant proportional loss of activity. Mitigation strategies involve using redox-active supports that facilitate the removal of poisons. For instance, CeO_2-based supports promote the decomposition of chlorinated compounds and the release of Cl_2, preventing the accumulation of chlorides [9]. Bimetallic systems (e.g., Pt-Pd) also demonstrate enhanced resistance, as the second metal can modify the electronic structure and adsorption energetics of the active sites [29].

Steam Deactivation occurs when water vapor a common by-product and component of industrial streams induces sintering or hydrothermal degradation of the support, leading to pore collapse and loss of surface area. For single-atom catalysts (SACs), hydrolysis of the metal-support bond can cause leaching or aggregation. Mitigation strategies include employing hydrothermally stable supports. Zeolites with high SiO_2/Al_2O_3 ratios and certain carbon-based materials exhibit superior resistance to steam. The exceptional stability of Pd single atoms on N-doped graphene, for example, is attributed to strong, covalent-like Pd-N_x bonding that resists hydrolysis [10].

By proactively designing catalysts with these deactivation pathways in mind through the strategic selection of supports and metal configurations the long-term operational stability of low-loading PGM systems can be significantly enhanced.

5. Performance in VOC Purification

The efficacy of low-loading PGM catalysts has been demonstrated across a range of representative VOCs. A key metric for evaluating catalytic activity is T_{90}, which is the temperature required to achieve 90% conversion of the target VOC. **Table 1** summarizes key performance metrics from recent studies.

The data in **Table 1** demonstrate that rationally designed low-loading catalysts can achieve performance comparable or even superior to that of conventional high-loading catalysts. The success hinges on the specific design principles: using SACs for maximized efficiency (e.g., Pt_1/CeO_2), employing redox-active supports for enhanced oxidation capability (e.g., Pd/MnO_2-Co_3O_4), utilizing confined en-

vironments for stability (e.g., Pt@Silicalite-1), and designing bimetallic systems or robust anchoring sites for harsh conditions (e.g., chlorinated VOCs).

Table 1. Performance of selected low-loading PGM catalysts in VOC oxidation.

Catalyst	VOC	Loading (wt%)	T_{90} (˚C)	Key Finding	Ref.
Pt_1/CeO_2	Formaldehyde	0.1	65	Isolated Pt atoms enable complete oxidation at room temperature.	[24]
Pd/MnO_2-Co_3O_4	Toluene	0.2	220	Synergy between Pd and mixed oxide support enhances oxygen mobility.	[9]
Pt@Silicalite-1	Propane	0.3	240	Zeolite encapsulation prevents sintering and improves hydrothermal stability.	[8]
Pt-Pd/CNT	Dichloromethane	0.5 (total)	320	Bimetallic system and CNT support resist chlorine poisoning.	[29]
Pd single-atom/N-doped Graphene	Benzene	0.15	190	Pd-N_4 sites show exceptional stability and water resistance.	[10]

6. Challenges and Future Perspectives

While mitigation strategies exist (Section 3.4), validating the long-term stability of ultra-dispersed catalysts under dynamic industrial conditions remains a critical challenge. A major hurdle is the industrial scalability of advanced synthesis methods like colloidal synthesis and single-atom catalyst preparation, as they often involve multiple steps, expensive reagents, or precise conditions that are difficult to maintain on a large scale [30] [31].

Future research should focus on:

Advanced In-situ/Operando Characterization: Utilizing techniques like environmental TEM, X-ray absorption spectroscopy, and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to understand the dynamic structure of active sites under reaction conditions [32].

Computational Guidance: Employing density functional theory (DFT) and machine learning to predict optimal metal-support combinations and design catalysts with tailored properties for specific VOCs [33].

Multi-functional Catalysts: Designing catalysts that can simultaneously handle complex VOC mixtures or combined pollutants (e.g., VOCs and NO_x) [34].

Sustainability and Circular Economy: Developing efficient methods for the recovery and recycling of PGMs from spent low-loading catalysts is crucial for the economic and environmental sustainability of this technology [35].

Comprehensive Life-Cycle and Techno-Economic Analysis: To fully assess sustainability, research must progress beyond laboratory metrics to include rigorous Life-Cycle Assessment (LCA) and Techno-Economic Analysis (TEA). LCA should quantify the environmental impact across the entire catalyst life cycle, from the potentially energy-intensive synthesis of advanced supports to end-of-life disposal. While reduced PGM content lowers the environmental footprint of mining and refining, this benefit must be evaluated against the resource costs of novel synthesis methods. Concurrently, TEA is required to validate the economic

argument. The drastic reduction in raw material costs must offset the potentially higher expenses of sophisticated supports and manufacturing, a balance that can be justified by demonstrating superior longevity and activity. Ultimately, proving a favorable economic and environmental balance over the full life cycle including efficient recycling of precious metals is crucial for industrial adoption and achieving genuine sustainability in air pollution control [35].

7. Conclusions

This review has highlighted significant advancements in the preparation of low-loading PGM catalysts for VOC purification. Through innovative synthesis strategies such as strong electrostatic adsorption, colloidal methods, and single-atom catalysis, it is possible to achieve exceptionally high metal dispersion and atomic efficiency. The critical role of the support material in stabilizing these active sites and participating in the catalytic cycle has been emphasized. When combined synergistically, these approaches yield catalysts with ultra-low PGM loadings that demonstrate excellent activity, selectivity, and, in some cases, enhanced stability for oxidizing various VOCs. While challenges in stability and scalable synthesis persist, the ongoing research in this field holds great promise for developing cost-effective and high-performance catalytic solutions, contributing significantly to sustainable air pollution control and environmental protection.

The rational selection of a support material is dictated by the specific VOC target. This alignment between support properties and pollutant class is key to designing high-performance catalysts:

Redox-active supports (e.g., CeO_2, MnO_2) with high oxygen storage capacity are ideal for oxidizing oxygenated VOCs (e.g., formaldehyde, alcohols) and aromatic hydrocarbons (e.g., toluene), as they readily supply active oxygen species.

Acidic supports (e.g., zeolites, Al_2O_3) are particularly effective for hydrocarbons (e.g., propane, alkenes) and chlorinated VOCs, as their acid sites facilitate the cracking and activation of these more stable molecules.

Conductive supports (e.g., carbon nanotubes, graphene) can enhance electron transfer, which is beneficial for redox cycles in the oxidation of various VOCs, while their tunable surface chemistry is advantageous for adsorbing aromatic and non-polar compounds.

By matching the inherent properties of the support to the chemical characteristics of the target pollutant, catalyst design moves from a trial-and-error approach to a rational strategy for efficient VOC purification.

Conflicts of Interest

The author declares no conflicts of interest.

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