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Ga-Pt bimetallic catalysts for propane dehydrogenation: Synergy, stability and strategies for industrial advancement: A literature review

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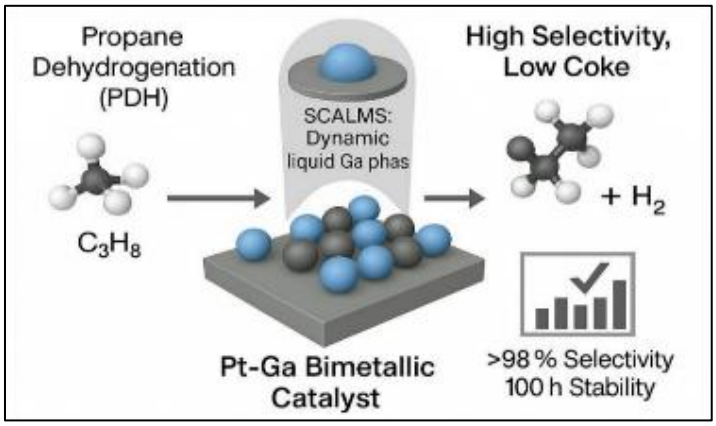
Abstract

The growing global demand for propylene, a key petrochemical feedstock, has intensified research into sustainable production methods beyond conventional cracking processes. Among emerging technologies, propane dehydrogenation (PDH) has gained prominence as a clean and direct route to propylene. This review critically examines the recent advances in gallium-platinum (Ga-Pt) catalysts, which have demonstrated exceptional performance in PDH. The synergy between Gallium and Platinum improves selectivity, suppresses coke formation, and enhances catalyst stability by isolating Platinum atoms and electronically modifying active sites. Developments such as single-atom intermetallics, Supported Catalytically Active Liquid-Metal Solutions (SCALMS), and electronic self-recovery mechanisms are discussed in detail. This review also explores advanced synthesis and characterization techniques, including Atomic Layer Deposition, X-ray Diffraction, Transmission Electron Microscopy, X-ray Photoelectron Spectroscopy, and operando spectroscopy, that elucidate active site structure and dynamics. Benchmarking data reveal Ga-Pt systems consistently outperform traditional Pt-Sn catalysts in activity, selectivity, and resistance to deactivation. The integration of machine learning and high-throughput screening has accelerated the design of next-generation catalysts. Finally, the industrial and environmental implications, challenges in scale-up, and future directions including ternary alloys and autonomous discovery platforms are addressed. This comprehensive analysis highlights Ga-Pt catalysis as a blueprint for rational catalyst design in PDH and beyond.

Graphical Abstract



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Keywords: Propane Dehydrogenation; Bimetallic Catalysts; Ga-Pt Synergy; Single-Atom Catalysis; DFT; Machine Learning

1. Introduction

The demand for propylene has sky-rocketed due to its recently acquired status as the most used petrochemical and polymer industry building block and this has created a widening difference between industrial production and its current demand. It has gained the interest of academia and industries which has led to numerous researches towards the direct manufacture of propylene from propane [1, 2].

Propylene serves as a crucial building block during the production of numerous polymers, fuels, and chemicals. A significant proportion of global propylene demand exists for the production of polypropylene through synthesis. Propylene is also used in the manufacturing of key compounds such as cumene, propylene oxide, acrylic acid, and isopropyl alcohol. In the petrochemical sector, propylene finds uses in the high-octane gasoline production as it aids in the processes of alkylation, catalytic polymerization, and dimerization [3].

This has led to the development of important production technologies, among which the catalytic dehydrogenation of abundant and low-cost propane (PDH) has become the best alternative. Propane dehydrogenation (PDH) is an important process for the production of propylene, which offers a clean way to dehydrogenate propane into propylene that is utilized in the manufacturing of plastics, synthetic materials, and other chemical products. With the growing need for propylene, PDH is in the front line of enhancing production efficiency as well as acting in fulfilling supply needs, while also offering an opening to overcome traditional Pt-based catalyst challenges such as deactivation and sintering [4,5,6]

This reaction however is associated with a high thermal absorption and demands that it is carried out under high temperature and low-pressure conditions which may enable the occurrence of side reactions like thermal cracking, leading to the light alkane formation and coke which are likely to produce rapid catalyst deactivation [7]. Achieving a high propylene selectivity and long-term stability at the high temperatures (550–700 °C) required for thermodynamically favorable conversion poses a challenge to this process.

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2 \qquad \Delta H_{293.15} = +124.3 \text{ kJ/mol} \qquad [8]$$

The majority of propylene has traditionally been produced as a byproduct of steam cracking and fluid catalytic cracking. These sources, however, have increasingly been unable to match the growing global demand. As a result, dedicated or "on-purpose" production technologies have been developed, particularly exploiting the availability of shale gas. Some of the leading commercial processes for light alkane dehydrogenation include CATOFIN (by CB&I and ABB Lummus), Oleflex (by UOP Honeywell), and the STAR process (by ThyssenKrupp Uhde) [9]. The current industrial catalyst landscape is dominated by chromium oxide ($CrOx/Al_2O_3$) and platinum-tin ($Pt–Sn/Al_2O_3$) systems. While cost-effective, chromium oxide catalysts pose environmental risks due to the toxicity of Cr(VI) and suffer from rapid coking, Platinum-based catalysts are highly active for C–H bond activation but, in their monometallic form, are notoriously unselective, promoting deep dehydrogenation, hydrogenolysis, and coking, which leads to rapid deactivation [10]. The addition of a second, non-noble metal promoter like tin (Sn) mitigates these issues by breaking up large Pt ensembles and modifying its electronic properties, forming the basis of technologies like the UOP Oleflex™ process [3].

In this review, the exploration of gallium (Ga) as a promoter for Pt has emerged as a particularly fruitful area of research. Early studies demonstrated that Ga could significantly enhance propylene selectivity and catalyst lifetime compared to both monometallic Pt and conventional Pt–Sn systems [11]. The Pt-Ga synergy creates an unparalleled catalytic efficiency that maximizes activity and long-term stability in propane dehydrogenation (PDH), augmenting activity and stability. Such effectiveness is a result of the singular interaction between Pt and Ga, which enhances the electronic structure and geometry of the catalyst. Such adjustments enhance hydrogen splitting and help resist coke formation, resulting in a more efficient and stable catalyst [12].

2. Basic Chemistry of Individual Metals

2.1. Gallium

In its metallic form or as an oxide (Ga_2O_3), gallium is largely inactive for propane C-H bond activation at typical PDH temperatures but supported gallium oxide has been studied as a catalyst for light alkane dehydrogenation [13]. Gallium

is more selective than Pt but its activity is generally too low for industrial application. This stems from the acidic and basic property of Gallium oxide catalyst which tends to greatly affect its catalytic activity and so, supported Gallium oxide catalyst tends to have a reduced acidity and is even more preferred than other catalysts [14].

2.2. Platinum

Platinum is exceptionally efficient at cleaving the strong C-H bonds in propane due to the favorable energy of its d-band center relative to the Fermi level, which facilitates strong interaction with hydrocarbon adsorbates [15]. However, this high reactivity tends to be of a great advantage. On the surface of Pt nanoparticles, contiguous multi-atom sites (ensembles) not only catalyze the desired first dehydrogenation step but also readily promote subsequent, undesired reactions such as

- Hydrogenolysis: This is where the strong C-C bonds in propane or propylene can be cleaved, leading to the formation of methane and ethane which is a direct loss of valuable product.
- Coking: The unsaturated surface species can polymerize and cyclize, eventually forming graphitic coke that physically blocks active sites and pores, causing rapid deactivation [16].

Consequently, a monometallic Pt/Al_2O_3 catalyst typically exhibits poor propylene selectivity (~80% or lower) and deactivates under industrial PDH conditions [17].

3. Ga-Pt Synergy

The remarkable performance of Ga-Pt catalysts arises from a complex interplay of effects that operate at different length scales, from atomic level electronic interactions to nanoscale structural dynamics. Table 1 summarizes the historical development of Ga-Pt PDH Catalysts

Table 1 Historical Milestones in the Development of Ga-Pt PDH Catalysts

Period	Representative Work & Formulation	Key Development/Outcome	Reference
Early 2000s	$Pt\text{-}Ga/Al_2O_3$ prepared by successive impregnation	First clear demonstration that adding Ga dilutes contiguous Pt sites, increasing propylene selectivity and slowing coking compared with monometallic Pt/Al_2O_3.	[18]
2010-2015	Ga-Pt "SCALMS" (Supported Catalytically Active Liquid-Metal Solutions)	Liquid Ga wets Pt nanoparticles; the mobile Ga phase continually renews the Pt–Ga interface, giving high activity and exceptional coke resistance.	[19]
2016-2019	Single-atom Pt locked in crystalline Pt-Ga intermetallic	Atomically isolated Pt in a Pt-Ga matrix shows >98% propylene selectivity for over 100 hours at 600 °C, illustrating the "single-site in alloy matrix" concept.	[20]
2020-2023	Electron-driven self-recovery of sub-nano PtGa clusters	Dynamic re-alloying under reaction conditions restores Pt–Ga ensembles; competitive adsorption on Pt-Gaδ+ sites lower the C–H activation barrier and suppresses deep dehydrogenation.	[21]
2023-2025	H_2-pretreatment & redox-swing strategies for Ga–Pt SCALMS	Mild H_2 treatment removes surface oxides, increases Ga^0 content, and doubles time-on-stream stability without causing sintering.	[22]

3.1. Electronic and Structural Interactions

The most fundamental synergistic effect is the geometric isolation of Pt atoms by Ga atoms. By substituting Ga into the Pt lattice, large, contiguous Pt ensembles are broken up and the remaining isolated Pt single atoms or small clusters are still active for the initial C-H bond splitting in propane but are hindered from catalyzing the subsequent reactions of adsorbed propylene that lead to coke formation. This effect is the primary reason for the dramatic increase in propylene selectivity [20,23].

Alloying Ga with Pt induces significant electronic modification. Density Functional Theory calculations consistently shows that Ga being more electropositive, donates electron density from its SP-band to the d-band of Pt. This charge transfer has two crucial consequences:

Down-shift of the Pt d-band center: The Pt d-band center is lowered by 0.25-0.35 eV away from the Fermi level. This weakens the adsorption energy of key intermediates, particularly propylene. While the bond to propane is weakened slightly, the bond to propylene is weakened more significantly. This facilitates rapid desorption of the desired product before it can undergo further reaction, thereby boosting selectivity.

Creation of Bifunctional Sites: The charge transfer results in slightly electron-rich Pt ($Pt^{\delta-}$) sites and partially positive Ga ($Ga^{\delta+}$) sites. This creates a bifunctional surface where Pt remains the primary center for C-H activation, while adjacent Ga sites can act as hydrogen acceptors or Lewis acid sites, potentially facilitating H-spillover and altering the reaction pathway [22,24].

3.2. Mechanistic Insights from Advanced Studies

Kinetics and DFT: Combined kinetic and computational studies have provided a detailed picture of the reaction mechanism. DFT calculations show that Ga incorporation can lower the activation barrier for the rate-limiting β-hydride elimination step by 0.1-0.2 eV, while simultaneously increasing the energy barrier for C-C cleavage [24]. This explains how Ga-Pt catalysts can be both more active and more selective than their Pt-Sn counterparts. The models also predict a significant reduction in the binding energy of carbonaceous species on Pt-Ga surfaces compared to pure Pt rationalizing the enhanced coke resistance [25].

In Situ/Operando Spectroscopy: The dynamic nature of Ga-Pt catalysts under reaction conditions has been revealed by powerful operando techniques. Operando Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) coupled with mass spectrometry has been used to monitor surface species and gas-phase products simultaneously. These studies have confirmed the electronic modification of Pt by observing a red-shift in the vibrational frequency of adsorbed CO, a classic indicator of increased electron back-donation from the metal [10]. Furthermore, operando studies have shown that proximal Ga^{+}-H^{+} pairs, formed during the reaction, are exceptionally active sites, exhibiting turnover frequencies up to 15 times higher than isolated Ga^{+} sites [26].

Dynamic and Liquid-Phase Behavior: A paradigm shift occurred with the introduction of Supported Catalytically Active Liquid-Metal Solutions (SCALMS). In this concept, solid Pt nanoparticles are suspended in a thin film of molten Ga on a support [19]. This fluidic environment continuously exposes fresh Pt-Ga active sites and is thought to dissolve or sweep away coke precursors, leading to extraordinary stability. More recent work has shown that even solid sub-nanometer Pt-Ga clusters exhibit dynamic behavior, undergoing "electron-driven self-recovery" where the alloy can de-alloy and re-alloy under redox cycles, maintaining high activity [21].

4. Catalyst Synthesis & Characterization

The specific architecture of the Ga-Pt interface is critical to its performance, and a variety of synthesis methods have been developed to control it.

4.1. Common Preparation Routes

Successive/Co-impregnation: The traditional method involves impregnating a high-surface-area support like γ-Al_2O_3 or ZSM-5 zeolite with aqueous solutions of Pt and Ga precursors (e.g., $[Pt(NH_3)_4]Cl_2.H_2O$ and $Ga(NO_3)_3$), followed by calcination and reduction. This method is simple but often leads to poorly controlled particle sizes and phase heterogeneity [27]

Atomic Layer Deposition (ALD): ALD offers layer-by-layer control over the deposition of Ga and Pt, enabling the synthesis of core-shell structures or finely dispersed alloys with unparalleled precision [28]

SCALMS Preparation: These catalysts are typically made by impregnating a support with Ga, followed by the addition of a Pt precursor. Upon heating, the Ga melts and dissolves the Pt, forming the active liquid film [19].

4.2. Advanced Characterization for Probing the Active Site

Characterization techniques employs the use of well-built devices in material science which enables researchers to analyze and understand the characteristics, properties and performances of various materials which ranges from

nanomaterials, solar cells, supercapacitors, and catalysts. The processes involved helps in unveiling the structural, chemical, and physical properties of materials necessary for optimizing their applications. Some characterization techniques employed includes X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), specific surface area measurements using the Brunauer–Emmett–Teller (BET) method, and X-ray Absorption Fine Structure (XAFS) analysis, X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption of ammonia (NH3-TPD), energy dispersive spectroscopy (EDS), thermogravimetric analysis (TG), [29,30,31].

4.2.1. X-Ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) is a standard technique that is widely applied in heterogeneous catalysis to determine the phase composition, atomic structure, and size of a materials crystals [32]. The XRD peaks result from the constructive interference of a monochromatic X-ray beam at the specified angle, as illustrated in the figure below [33]. However, the position, intensity, and width of the peak mostly depend on the characteristics of the atomic structure. It applies the principle of diffraction, where X-rays interact with the atoms in the crystal lattice of the material and produces a diffraction pattern that provides important information which aids the identification of a material's structure.

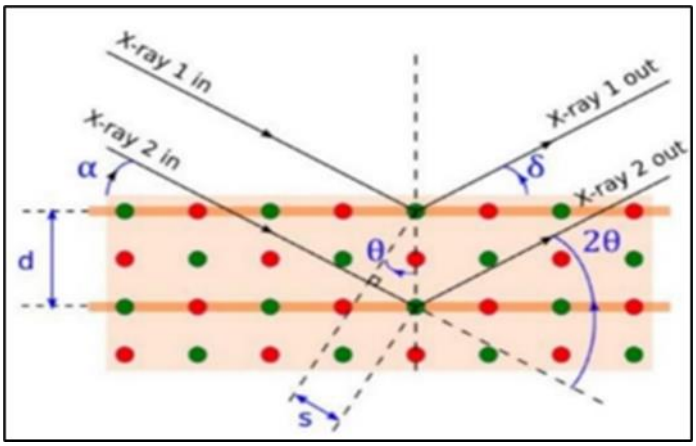

Figure 1 Phenomenon of constructive interference observed during X-ray diffraction (XRD) [34]

4.2.2. Bragg's Law and Diffraction Principle

The Bragg's Law, which describes the conditions for constructive interference of X-rays diffracted from crystal planes. Bragg's Law is expressed as:

$$d = \frac{n\lambda}{2sin\theta}$$

where: n is an integer (order of diffraction),
λ is the wavelength of the X-rays,
d is the interplanar spacing between atoms in the crystal lattice,
θ is the angle of incidence and diffraction [35].

This law explains how X-rays diffracted from different atomic planes interfere constructively when the path difference between the waves is an integer multiple of the wavelength [36].

4.2.3. X-ray Generation and Instrumentation

X-rays are produced using an X-ray tube, where high-energy electrons strike a metal target (e.g., copper or molybdenum) and produces X-rays of a given. An XRD device consists of an X-ray Source, a Collimator, Sample Holder and a detector [37].

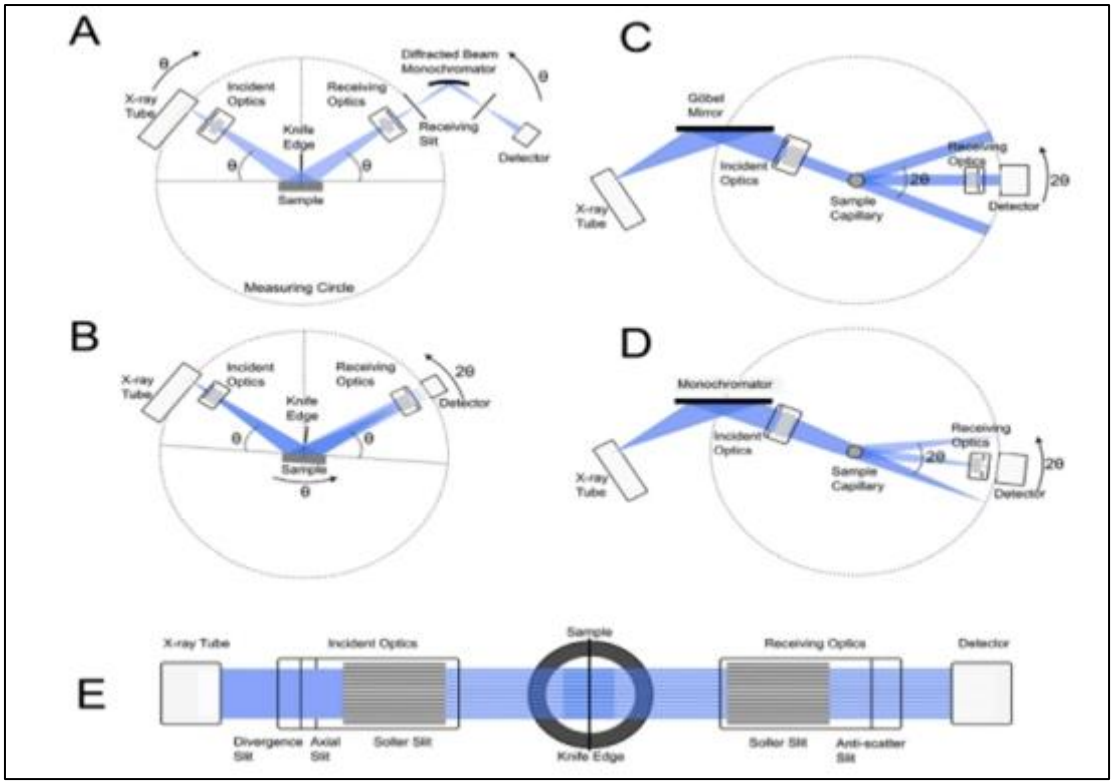

Figure 2 A Schematic representation of a basic Bragg-Brentano (BB) instrument configuration, angular resolution is determined by the receiving slit opening and the radius of the measuring circle [38]

4.2.4. Diffraction Pattern and Analysis

On interaction with a crystalline sample, X-rays diffract at specific angles and creates a diffraction pattern which is a blueprint of the material's crystal structure and the various peak positions and peak intensities helps us understand the Phases present, the crystal Structure, structural Parameters such as grain size, strain, and defects [39].

XRD is most effective for materials with a well-defined crystal structure and provides limited information for amorphous substances. This technique requires careful sample preparation, especially for thin films and nanomaterials [40].

4.2.5. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a research method that enables researchers to study a specimen's surface topography and chemical composition. However, in its simplest form, it uses a beam of electrons and SEM interacts with some atoms of the sample to emit some signals and information obtained from the signals can serve to provide the important information of the material characteristics and arrangement.

By adjusting the control of the electron beam, material density differences in the sample can be examined precisely. This technique is remarkable due to its broad application in multiple sectors, ranging from materials science to semiconductor manufacturing to research in biology. The combination of high-resolution images with precise compositional information at the same times makes SEM especially useful for failure analysis, quality control as well as more complex scientific inquiries [41,42,43]

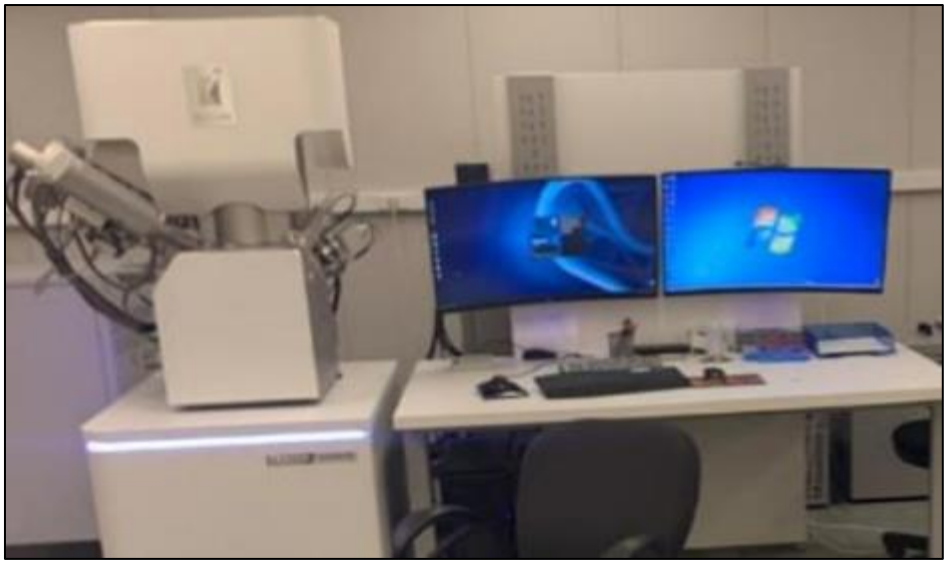

Figure 3 SEM (at MISIS university)

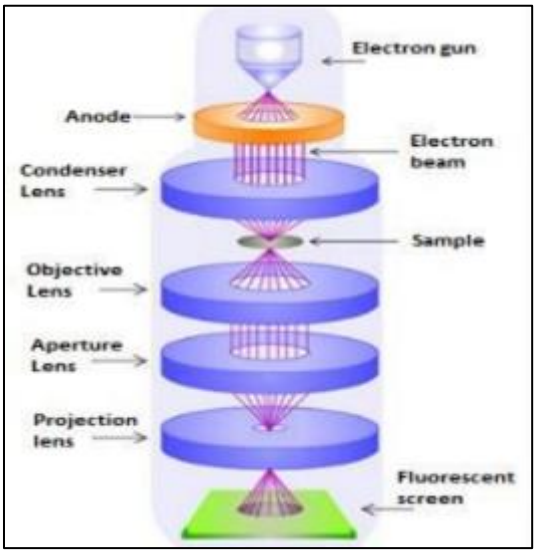

Figure 4 Schematic diagram of the scanning electron microscope [44].

4.2.6. Transmission Electron Microscopy (TEM)

The transmission electron microscopy or TEM for its acronym in English, is a visual analytical technique which uses an electron beam, positioned on a sample to get a magnified version of the material over a fluorescent screen [45]. TEM has been applied and used for both structural and morphological characterization of different materials as well as catalysts as it supplies detailed information about the size, shape, and distribution of nanoparticles which are necessary fundamentals for understanding the behaviors of materials as well as a material catalytic activity [46].

TEM has generally been used for studying the morphology of nanomaterials, nanomaterials-polymer interface, microanalysis by characteristic X-rays, localized chemical composition of nanomaterial or thin film, electron diffraction patterns, In situ temperature changes in the sample, differentiating phases of nanomaterials by using electron energy-loss spectroscopy, chemical mapping of an area of interest of the sample, live dynamics of the nanomaterials in liquid phase by using latest liquid-cell TEM holder [47]. A drawback of this technique is that it is time consuming and proceeds with little efficiency in terms of the preparation of the sample due to financial constraints [45].

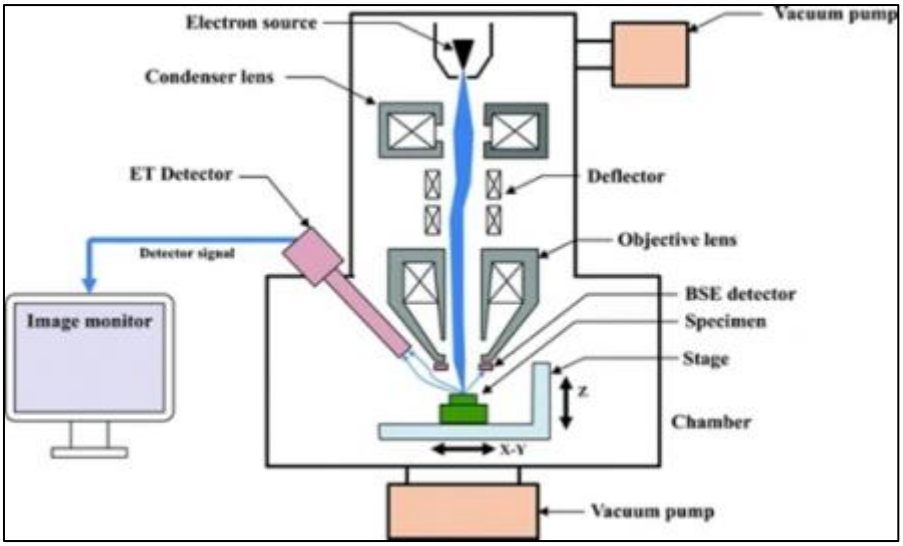

Figure 5 Transmission electron microscope Illustration [45]

4.2.7. X-Ray Photoelectron Spectroscopy (XPS)

XPS has found great application in surface analysis of materials cutting across areas such as corrosion, catalysis, electronics, nanomaterials, biomedicine, mineral processing, automotive and aerospace etc. Most often, the technique is used to obtain the chemical composition, surface functionalization, adsorbates, layer thickness and in some cases even particle size of nanomaterials [48].

It employs the use of X-rays which knocks off photoelectrons from a material and then measures the kinetic energy of the photoelectrons. This kinetic energy measured allows researchers to determine the binding energies of the electrons which are specific to different elements and their chemical environments. The technique is particularly useful for analyzing surfaces and thin films and this makes XPS ideal for studying surface phenomena such as corrosion, catalysis, and the properties of nanomaterials [49,50]. This method of spectroscopic analysis can be used to confirm the presence of all elements with exception to hydrogen and helium which have detection limits ranging between 0.1%–1% approximately. XPS is extremely surface sensitive and so necessary care needs to be employed to avoid surface contamination [51].

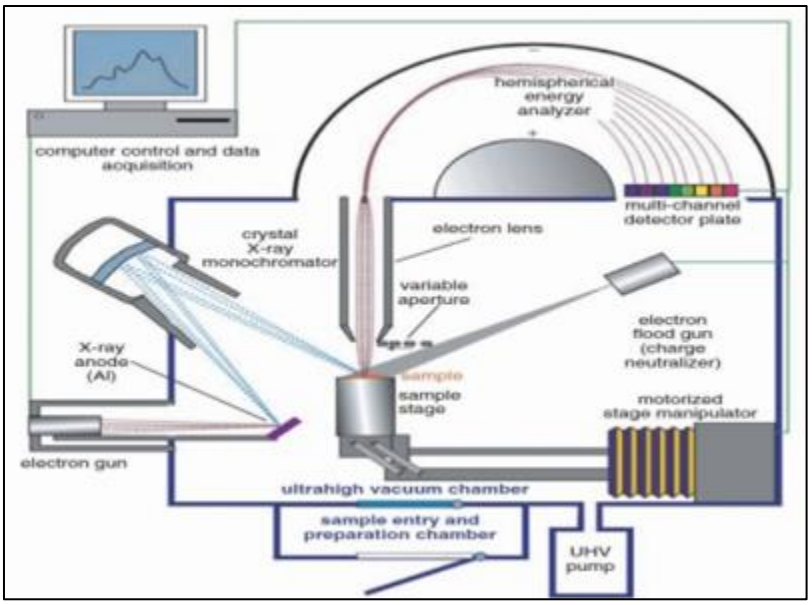

Figure 6 Schematic view of the XPS instrumentation [52]

4.2.8. The Brunauer-Emmett-Teller (Bet) Method

The BET method is a major technique applied to access and measure the specific surface area of materials (porous materials) more especially solids which may be amorphous in nature like activated carbons or may possess crystalline structure like metalorganic frameworks (MOFs) and covalent organic frameworks (COFs) [53]. The specific surface area of a material is an essential characteristic that impacts its performance in applications such as catalysis, gas adsorption, and chemical reactions. This technique enables the measurement of the surface area of materials with precision and consistency and is used greatly in scientific, industrial, and quality assurance fields. The BET method begins by an exposure of the solid material to a gas at a known temperature and pressure which is increased gradually with the quantity of adsorbed gas recorded at each pressure attained. The data obtained are then used to plot the BET isotherm which is a graph of the amount of adsorbed gas (typically nitrogen) against the relative pressure and the characteristic shapes and linear region at intermediate pressures obtained is utilized for analysis [54].

4.2.9. The BET theory

The fundamental element of the BET theory is associated with the adsorption of a gas on the material's surface. The working principle of the BET is derived from the Langmuir theory of multi-layer adsorption of gas molecules on a solid surface [55]. This theory is rooted on some assumptions that may not be ideal for determining the surface area of microporous materials such as MOFs and has such intrigued the curiosity of many researchers who have delved into the investigation of the suitability of this method [56]

The assumptions of the BET theory are as adopted from [55,57] are

- Adsorption occurs on a uniform/homogeneous surface and all the gas molecules in the first adsorbed layer have equal energies of adsorption,
- The uppermost molecules in adsorbed stacks are in dynamic equilibrium with the vapor,
- The differential energy of physisorption for the first layer, E1 is higher than the heat of liquefaction, EL,
- There is no lateral interaction between adsorbate molecules in the same layer, and
- The second and subsequent layers formation start before the completion of the first layer.

It has been observed that the effective predictability of the number of adsorbate molecules available in the outermost covering of the solid guarantees the success of these assumptions.

Operando DRIFTS: As mentioned, this technique links surface chemistry with catalytic activity in real-time. For example, in a study of La-promoted $PtGa/Al_2O_3$, operando DRIFTS showed that the presence of lanthanum facilitated faster removal of surface hydrogen, which correlated with a lower rate of coke formation observed by thermogravimetric analysis (TGA) [26]. The combination of these techniques provides a powerful "triangulation" method, correlating atomic structure (STEM), electronic state (XAFS), and surface reactivity (DRIFTS) with macroscopic performance (activity, selectivity, stability).

5. Performance Benchmarking

The ultimate measure of a catalyst's utility is its performance relative to established and emerging alternatives. Ga-Pt systems, particularly the newer generations, consistently outperform traditional Pt-Sn catalysts and are highly competitive with other advanced bimetallic systems like Pt-Zn.

Table 2 Comparative Performance of Representative Bimetallic PDH Catalysts

Catalyst System	Typical Conversion / Activity	Propylene Selectivity	Stability Notes	Key Reference
$Pt\text{-}Sn/Al_2O_3$ (Conventional)	30% C_3H_8 conversion (64.1 μmol g^{-1} h^{-1})	Moderate	Deactivates gradually via coking and sintering; Sn only partially mitigates these issues.	[10]
Pt-In (Pt_3In) (DFT-guided)	"Considerable improvement" over pure Pt	High	Alloying lowers ΔE for β-H elimination while disfavoring	[24]

			C-C cracking, implying slower deactivation. Experimental data is limited.	
Pt-Zn (Single-site)	High activity at 550-620 °C	>99%	Excellent stability due to strong Pt–ZnO_x interfacial interaction, which prevents sintering and coking.	[25]
Pt-Ga (Single-atom intermetallic)	"Ultrastable" with high activity >600 °C	>98% (near-quantitative)	Maintains activity for >100 h with negligible coke due to rigid isolation of Pt atoms in the Ga matrix.	[20]

5.1.1. Analysis of Benchmarking Data

Selectivity: The most significant advantage of advanced Ga-Pt and Pt-Zn catalysts is their exceptional propylene selectivity, which often exceeds 98-99%. This is a substantial improvement over Pt–Sn, where selectivity is typically lower due to residual cracking activity. The near-quantitative selectivity of single-atom Pt-Ga and single-site Pt-Zn catalysts represents the current state-of-the-art, minimizing feedstock loss and simplifying downstream separation processes [25,20].

Activity: While Pt–Sn shows moderate activity, both Pt-Ga and Pt-Zn intermetallic or single-site catalysts exhibit high turnover frequencies at industrial temperatures. This is attributed to the optimized electronic structure that lowers the C-H activation barrier without promoting C-C cleavage channels.

Stability: This is where the new generation of catalysts truly shines. The rigid intermetallic lattice of Pt-Ga physically prevents Pt atoms from migrating and sintering, even at temperatures above 600 °C. This leads to ultra-stable performance for over 100 hours with negligible deactivation [20]. Similarly, the strong interfacial anchoring in Pt-ZnO_x systems imparts excellent resistance to sintering and coking [25]. In contrast, Pt-Sn catalysts still require frequent regeneration cycles to burn off coke [10].

In summary, Ga-Pt catalysts, especially in their single-atom intermetallic form, set the benchmark for combining high activity, near-perfect selectivity, and outstanding coke-free stability, making them a highly promising candidate for next generation PDH processes.

6. Deactivation and Regeneration

Despite their enhanced stability, all Ga-Pt catalysts are susceptible to deactivation over long operational periods. Understanding these mechanisms is crucial for designing robust industrial processes.

6.1. Deactivation Mechanisms

The primary deactivation modes are coking and changes in the alloy structure, as detailed in Table 3.

Table 3 Deactivation Mechanisms and Regeneration Strategies for Ga-Pt Catalysts

Deactivation Mode	Microscopic Origin	Consequence	Regeneration Strategy	Principle & Conditions
Coking	Excessive dehydrogenation of propyl/propylene intermediates, followed by cyclization and polymerization on both metal and support sites.	Rapid activity drop, especially during the first few hours on-stream. Even highly stable SCALMS catalysts show measurable rate loss due to coke (e.g., 0.5 wt% after 3h at 600°C) [19,16]	Oxidative Burn-off + Reduction	Air at 550-600°C to burn coke, followed by H_2 at 550°C to re-reduce and re-alloy the metals. Can restore >90% of initial activity [58]
Sintering/ Segregation	Mobility of Pt atoms at high temperatures (>600°C) and potential	Irreversible loss of isolated Pt–Ga ensembles, leading to a	Mild H_2 Pretreatment	H_2 flow at ~600°C removes soft coke via hydrogenolysis.

	Ga loss or segregation, leading to the growth of Pt-rich particles.	decline in selectivity and activity. HAADF-STEM shows particle growth from ~1 nm to >4 nm after 16h [59]		Restores 80% activity for SCALMS with negligible particle growth [22]
Ga Loss/Volatility	Formation of volatile Ga_2O or $GaCl_x$ species during high-temperature regeneration cycles.	Gradual change in the Ga/Pt stoichiometry, leading to a slow decline in selectivity over many cycles. Requires periodic Ga make-up.	Self-Healing (SCALMS)	The liquid Ga layer continuously renews the active interface, dissolving or displacing coke precursors. Coking rate is ~3x lower than conventional Pt-Ga/Al_2O_3 [19]

6.2. Industrial Implementation Challenges

Translating the excellent lab-scale performance of Ga-Pt catalysts to industrial reality presents several significant hurdles:

Regeneration Control: The standard industrial regeneration process involves oxidative coke burn-off in a continuous catalytic regeneration (CCR) unit. This process must be carefully controlled to avoid over-oxidation of the metals, which can accelerate Pt sintering and lead to the formation of volatile gallium sub-oxides, permanently altering the catalyst [58].

Irreversible Sintering: While ordered inter-metallics are highly resistant, less-defined alloyed nanoparticles can still sinter over repeated high-temperature cycles. Once large Pt-rich particles form, they are difficult to redisperse without resorting to harsh, corrosive treatments (e.g., oxy-chlorination), which are environmentally and operationally undesirable [59].

SCALMS Scale-Up: The innovative SCALMS concept faces major engineering challenges. Handling large volumes of molten gallium in packed-bed reactors raises concerns about liquid channeling, pressure drop instability, and the potential for Ga to bleed from the support and condense in cooler downstream equipment [19].

7. Emerging Design Principles & Framework

The wealth of fundamental knowledge on Ga-Pt synergy is now converging with powerful computational tools to create a new, predictive framework for catalyst design. The focus is shifting from simply combining elements to precisely engineering the atomic and electronic structure of the active site.

7.1. From Random Alloys to Defined Structures

The field has clearly moved beyond randomly dispersed bimetallic nanoparticles. The key design principle is the creation of isolated, electronically-modified Pt sites. This can be achieved through:

Ordered Inter-metallics: Synthesizing crystalline phases like Pt-Ga, where the crystal structure itself dictates the isolation of Pt atoms, providing maximum selectivity and stability [20].

Single-Atom Catalysts (SACs): Dispersing individual Pt atoms on a Ga_2O_3 support or creating Pt_1-in-Ga liquid alloys to maximize atom efficiency and enforce the ensemble effect.

Ternary Systems: Introducing a third component, such as CeO_2 or La_2O_3, can provide additional functionality. For instance, CeO_2 can act as an oxygen buffer to facilitate coke removal, while La^{3+} can anchor Ga species, preventing their migration and improving long-term stability [60]

7.2. Machine Learning and High-Throughput Approaches

The compositional and structural space for bimetallic and multimetallic catalysts is vast. Exploring it experimentally is infeasible. Machine learning (ML) and high-throughput (HT) screening are emerging as transformative tools to accelerate discovery [61].

Table 4 Recent Advances in Machine Learning-Guided Design of PDH Catalysts

Year / Ref.	ML Strategy	System Studied	Key Outcome
2022 [62]	Gradient-boosted decision tree (trained on DFT data)	Pt-M (M = 31 metals)	Rapidly screened 510 Pt_3M surfaces to predict C–H activation barriers, identifying Pt_3In and Pt_3Sn as top candidates, which were later validated experimentally. -
2023 [63]	Graph convolutional neural network (GCNN) + HT-DFT	Pt–M dual-atom catalysts (DACs) on γ-Al_2O_3	Screened ~3,000 DACs for propane adsorption/dehydrogenation energetics, identifying 14 promising candidates. Synthesized Pt-Co, Pt-Zn, and Pt-Ga DACs showed >94% propylene selectivity.
2024 [24]	Probability-based screening (Logistic Regression)	Pt_xIn_γ alloys	Predicted Pt_3In as a Pareto-optimal composition balancing activity and stability criteria. Subsequent experiments showed a 6% higher TOF than industrial Pt-Sn. -
2024 [64]	Bayesian optimization + robotic synthesis	Pt-M oxides (oxidative PDH)	Created a closed-loop, autonomous workflow that improved propylene yield by 42% relative to the baseline after only six experimental cycles. -

These studies show that ML can effectively learn the complex composition-structure-property relationships in bimetallic catalysts. By training models on DFT-calculated data (e.g., adsorption energies, activation barriers) or experimental results, researchers can pre-screen thousands of candidates and prioritize the most promising ones for synthesis, reducing the experimental workload by over 85% in some cases [65].

8. Industrial and Environmental Implications

The advancements in Ga-Pt catalysis have significant potential for industrial and environmental benefits.

Economic Viability: Higher propylene selectivity (>98% vs. ~90% for older technologies) directly translates to higher yield per pass and less wasted propane feedstock. The exceptional stability of single-atom Pt-Ga catalysts could dramatically extend the time between regeneration cycles from hours to weeks or months, significantly increasing plant uptime and productivity. This reduces the operational costs associated with the energy-intensive regeneration process.

Environmental Footprint: Reduced coking means less frequent oxidative burn-off, lowering the overall CO_2 emissions from the plant. Higher selectivity also reduces the formation of byproducts like methane and ethane, which are either flared (producing CO_2) or require energy-intensive separation. The move towards highly active single-atom catalysts also reduces the total amount of precious platinum required, lowering both cost and the environmental impact of mining [61,66]

Scalability: While promising, the scalability of the most advanced synthesis methods (e.g., ALD, SOMC) and catalyst concepts (e.g., SCALMS) remains a key challenge that must be addressed before widespread industrial adoption.

9. Future Research Directions and Knowledge Gaps

Despite tremendous progress, several key areas require further investigation to fully realize the potential of Ga-Pt and other advanced bimetallic catalysts.

Exploring Complex Alloys: The focus is expanding from bimetallic to ternaries (e.g., Pt-Ga-X) and high-entropy alloys. ML-guided screening will be essential to navigate this vast compositional space to find promoters that further enhance stability or reduce the required Pt loading.

Dynamic Behavior under Operation: Most characterization and modeling still focus on the catalyst in its pristine or post-reaction state. More research using operando techniques is needed to understand the dynamic restructuring, phase segregation, and self-healing mechanisms of catalysts like SCALMS and sub-nano clusters during the reaction.

Bridging the Pressure and Materials Gap: DFT studies are often performed on idealized single-crystal surfaces under vacuum. Efforts to model more realistic, amorphous-supported nanoparticles under reaction pressures are needed to improve the predictive power of computational screening.

Autonomous Discovery Platforms: The integration of ML, robotic synthesis, and high-throughput characterization into closed-loop, self-driving laboratories promises to revolutionize catalyst discovery, enabling rapid optimization of catalyst formulations for specific process conditions [64].

Industrial Patent Landscape: A notable gap in the publicly indexed literature is a clear mapping of the industrial patent landscape. While academic research is abundant, a dedicated search of patent databases would be required to understand which Ga-Pt formulations are being actively pursued for commercialization by major chemical companies and technology licensors [20].

Explainable AI (XAI): As ML models become more complex, it is crucial to develop XAI methods to extract human interpretable design rules from them. This will not only build trust in the predictions but also deepen our fundamental scientific understanding of what makes a good catalyst [67].

10. Conclusion

The advancement of Ga-Pt catalysts represents a significant breakthrough in the field of propane dehydrogenation, offering an effective solution to the challenges of selectivity, deactivation, and catalyst longevity. Through precise control of atomic structure and electronic interactions, these bimetallic systems exhibit superior performance compared to conventional Pt-Sn catalysts, particularly in suppressing coke formation and maintaining high propylene yields over extended operation. Innovations such as single-atom alloys, intermetallic compounds, and SCALMS have expanded the frontier of catalyst design, enabling both fundamental understanding and practical improvements.

Moreover, the integration of advanced characterization techniques and machine learning accelerates the discovery and optimization of next-generation PDH catalysts. Despite remaining industrial hurdles such as scalability, regeneration control, and economic viability the Ga-Pt platform provides a compelling foundation for sustainable, high-efficiency olefin production. Continued research into dynamic behavior under reaction conditions, complex alloy systems, and autonomous synthesis strategies will be essential to bridge the gap between laboratory performance and real-world application.

Compliance with ethical standards

Disclosure of conflict of interest

The authors confirms that they have no identifiable conflicts of interest, financial interests, or personal affiliations that could have influenced the research reported in this article.

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