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Advances in Zeolite-Encapsulated Platinum-Based Catalysts for Propane Dehydrogenation

Ziyang Zhou

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, China
zhziyang2024@lzu.edu.cn

Abstract. Propane Direct Dehydrogenation (PDH) represents the dominating technique for propylene synthesis, a research hotspot in modern coal chemical and light hydrocarbon engineering. Pt-based catalysts manifest intrinsic superiority in C-H bond cleavage, while zeolites endow unique spatial confinement, tunable acid-base properties and strong metal-support interactions, which modulate Pt electronic states and particle dispersion, thus suppressing coke deposition and thermal sintering. This review systematically dissects the molecular-level dehydrogenation mechanism of Pt-zeolite catalysts, clarifying the intricate structure-activity relationships among active site micro-configuration, surface electronic effects, and reaction pathways. It further provides a comprehensive comparative evaluation of two mainstream synthetic strategies, post-synthetic modification and in-situ one-pot crystallization, focusing on their efficacy in the precise fabrication of subnanometric Pt active sites and the long-term catalytic durability of the resulting materials. Finally, we summarize the pivotal scientific insights and technical progresses achieved in this field, laying a solid theoretical foundation for the rational design and industrial upgrading of high-efficiency, stable PDH catalysts.

Keywords: Heterogeneous catalysis, Pt, zeolite, propane dehydrogenation

1. Introduction

The demand for propylene, a pivotal feedstock in plastics, textiles and other fields, has sustained rapid growth. Conventional propylene production processes suffer from high feedstock dependence and cost volatility, limiting their applicability. With the abundant supply of propane, Propane Dehydrogenation (PDH) has emerged as an industrial focus due to its feedstock availability, process simplicity and cost controllability [1]. PDH is categorized into Oxidative Dehydrogenation (OPDH) and direct dehydrogenation (PDH). OPDH, using oxidants such as CO_2 or O_2, overcomes thermodynamic constraints with low-temperature exothermic reactions, but metal oxide catalysts (e.g., MnO_x, CoO_x) suffer from poor propylene selectivity, product deep oxidation and separation challenges, hindering industrialization [1]. In contrast, PDH exhibits superior propylene selectivity and yield, holding broad industrial prospects.

Traditional and commercial PDH catalysts mainly include the following types: Platinum (Pt) -based catalysts and Chromium (Cr) -based oxide catalysts. At present, in actual production, Pt-Sn alloys and CrO_x series oxide catalysts are the most mature and stable systems. CrO_x catalysts are widely used due to their low cost and solid industrial foundation, but their environmental toxicity and high-temperature stability remain challenges. In contrast, Pt-zeolite catalysts show unique and powerful advantages. First, the Pt species as the active center has an extremely strong ability to activate C-H bonds, which can efficiently break C-H bonds in propane molecules and facilitate the initiation and progress of dehydrogenation reactions. The regular and ordered microporous structure of the zeolite carrier can not only provide uniform dispersion sites for the Pt active component to prevent Pt particle agglomeration sintering, but also inhibit the formation and growth of carbon deposit precursors through the spatial confinement effect, significantly extending the catalyst life [2]; On the other hand, the abundant acidic sites on the zeolite surface can work synergistically with the Pt active center to regulate the adsorption-desorption behavior of reactants and products, significantly improving the selectivity for propylene and reducing the occurrence of side reactions such as deep dehydrogenation and cracking of propane [2]. These outstanding advantages make Pt-zeolite catalysts show broad industrial application prospects in PDH reactions and become core candidate systems to replace traditional catalysts.

Herein, this review summarizes recent advances in zeolite-supported Pt-based PDH catalysts. We elaborate on the microscopic mechanism of Pt-catalyzed PDH, focusing on key steps including propane C-H bond activation, propylene desorption and coking inhibition. Furthermore, we compare the effects of diverse synthesis methods on Pt dispersion, support stability and catalytic performance, providing insights for the rational design and industrial application of high-efficiency PDH catalysts.

2. Reaction mechanism

The core reaction pathway of Pt-catalyzed PDH, confirmed by theoretical calculations and experiments, follows the Horiuti-Polanyi (H-P) stepwise dehydrogenation mechanism (Figure 1) [3]. Propane undergoes reversible C-H bond activation on Pt surfaces via a cycle of "adsorption-activation-intermediate transformation-product desorption-surface regeneration". As a saturated alkane, propane adsorbs physically on Pt through weak C-H···Pt σ-π interactions (adsorption energy: -20 to -40 $kJ\cdot mol^{-1}$). The Rate-determining Step (RDS) is the first C-H bond cleavage ($CH_3CH_2CH_3 \rightarrow C_3H_7^* + H^*$) with an energy barrier of 80-120 $kJ\cdot mol^{-1}$, attributed to the high C-H bond energy (~410 $kJ\cdot mol^{-1}$) and configuration reconstruction cost. Low-coordination Pt step sites stabilize the transition state via strong orbital overlap, reducing the barrier by 20-30 $kJ\cdot mol^{-1}$, whereas high-coordination terrace sites exhibit lower activity. The $C_3H_7^*$ intermediate undergoes rapid β-H elimination (barrier: 30-50 $kJ\cdot mol^{-1}$) to form $C_3H_6^*$. Propylene adsorbs moderately on Pt (-60 to -80 $kJ\cdot mol^{-1}$), ensuring thermodynamic driving force for β-H elimination while enabling rapid desorption—this balance underpins the high propylene selectivity (>90%) of Pt-based catalysts. Surface H* desorbs as H_2 (barrier: 20-40 $kJ\cdot mol^{-1}$), with low H coverage facilitating active site regeneration and high coverage causing "hydrogen blocking" and promoting side reactions [4].

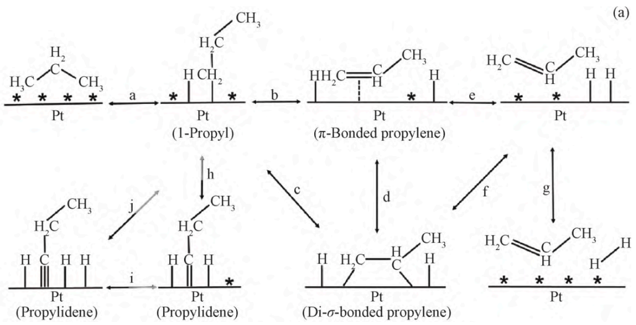

Figure 1. Mechanism diagram of propane dehydrogenation reaction [3]

PDH selectivity competition arises from the interplay between the H-P pathway and side reactions (deep dehydrogenation, C-C cleavage, coking). These side reactions are favored by large Pt ensembles (>3 Pt atoms) or high-coordination sites, which enhance unsaturated intermediate adsorption and C-C bond cleavage. Diluting Pt ensembles with alloying elements (e.g., Sn) or increasing low-coordination sites regulates surface electronic structure and suppresses multi-atom synergy, mitigating side reactions and coking.

3. Preparation methods of PT-based catalysts supported on zeolites: post-synthesis and one-pot synthesis

3.1. Post-synthesis method

Post-synthesis introduces Pt species into formed zeolites by means of impregnation, ion exchange, etc. The type of Pt precursor, the acidity and pore structure of the zeolite, and the calcination reduction process can all affect the final structure and dispersion state of Pt.

3.1.1. Impregnation method

Impregnation is the industrial mainstream for Pt-based catalyst synthesis due to its simplicity and scalability. For Pt-based bimetallic/polymetallic systems, achieving high Pt dispersion and intermetallic synergy is critical for PDH performance [5-7]. Liu et al [8] used tetra-butylammonium hydroxide as the template agent to synthesize the zeolite nanosheet SP-S-1 from the column support, and introduced Pt and Zn successively through stepwise impregnation; The ZnO_x-Si structure formed by the bridging of the unit point Zn^{2+} with the carrier Si-OH can effectively anchor Pt species and facilitate the formation of highly dispersed Pt clusters (Figure 2). The unique structure of the SP-S-1 support not only enhances the mass transfer diffusion effect but also significantly improves the accessibility of the active center Pt, ultimately resulting in a high specific activity of 1.23 $mol_{C_3H_6}$ g^{-1} h^{-1} and a high propylene selectivity of 99% compared to the conventional S-1 zeolite supported catalyst. There was no significant deactivation after 90 hours of continuous reaction (Figure 3).

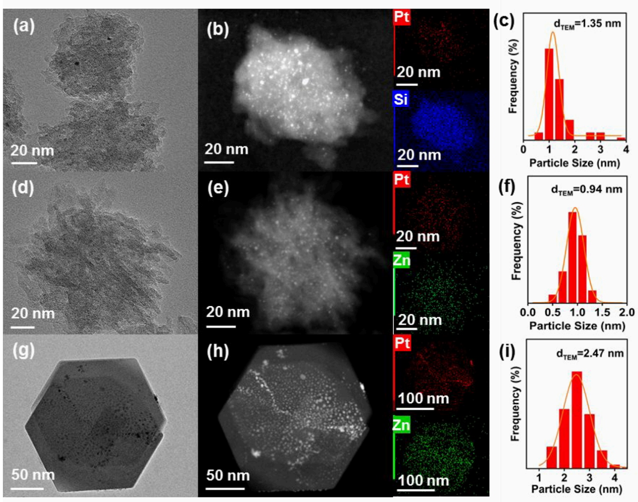

Figure 2. TEM images, STEM and EDS mapping, and particle distribution of the reduced catalysts: (a–c) Pt/SP-S-1, (d–f) PtZn/SP-S-1, and (g– i) PtZn/S-1 [8]

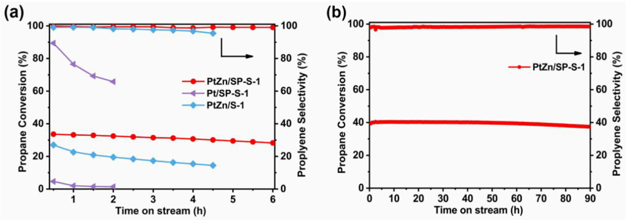

Figure 3. Propane conversion and propylene selectivity as a function of reaction time over (a) PtZn/SP-S-1, Pt/SP-S-1, and PtZn/S-1 (reaction conditions: T = 580°C, WHSV = 180 h-1, P = 1 atm, pure C3H8) and (b) PtZn/SP-S-1 (reaction conditions: T = 580°C, WHSV = 15 h-1, P = 1 atm, pure C3H8) [8]

Zhu et al. [9] prepared multiporous carriers rich in micropores and mesoporous by desilicalizing high-silicon ZSM-5 zeolites with an alkaline solution; The highly dispersed PtSn bimetallic nanoparticles were then confined and encapsulated in the mesoporoids of the ZSM-5 zeolite by sequential impregnation of hexane solution with organomemetallic salt Bu_3SnH and toluene solution with $Pt(COD)Me_2$ at 150°C hydrogen reduction (synthetic route shown in Figure 4). STEM characterization showed that the average size of PtSn bimetallic nanoclusters in the multi-level pore ZSM-5 was only 1.33 nm, and the mesoporous structure had a significant stabilizing and confining effect on PtSn nanoparticles; The $PtSn_{1.00}$/ZSM-5 (0.8) catalyst exhibited optimal PDH performance at 570°C, with an initial propane conversion rate of 46% and a propylene selectivity of 98% (Figure 5). All of the above studies confirmed that by regulating the pore structure and surface active sites of multi-level pore zeolites, high dispersion and stable loading of Pt-based species could be achieved, thereby simultaneously enhancing the activity, selectivity and stability of PDH reactions.

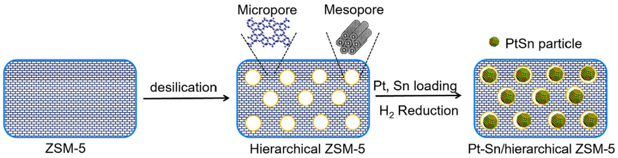

Figure 4. Synthesis procedure for PtSnx/ZSM-5 catalysts [9]

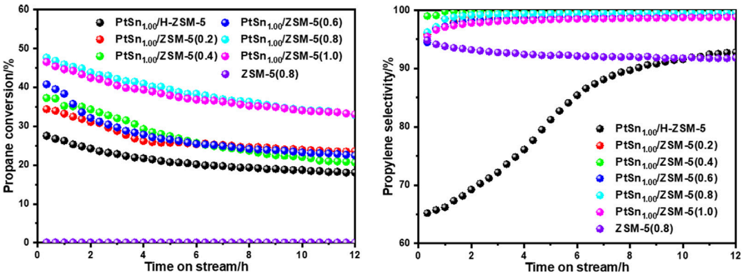

Figure 5. Propane conversion and propylene selectivity of different $PtSn_{1.00}$/hierarchical ZSM-5(y) catalysts and the ZSM-5(0.8) sample during propane dehydrogenation at 570°C [9]

3.1.2. Ion exchange method

Ion exchange is a common method of introducing metal cations into silica-alumina zeolites, balancing the negative charges of the zeolite skeleton through cations, and achieving the encapsulation of metal species after high-temperature treatment. It is important to note that during the ion exchange process, the pH of the solution must be precisely controlled to prevent the precipitation of metal cations on the outer surface of the zeolite carrier [10]. Iida et al. [11] used a Zn-structured MFI zeolite (Zn-MFI) as the carrier and ion-exchange it with Pt $(NH_3)_4(NO_3)_2$ aqueous solution, followed by calcination treatment to introduce Pt species into the zeolite; During the calcination process, Zn in the zeolite skeleton undergoes demetallization and reacts in situ with Pt species to form a PtZn bimetallic alloy with a particle size distribution concentrated around 1nm (Figure 6).

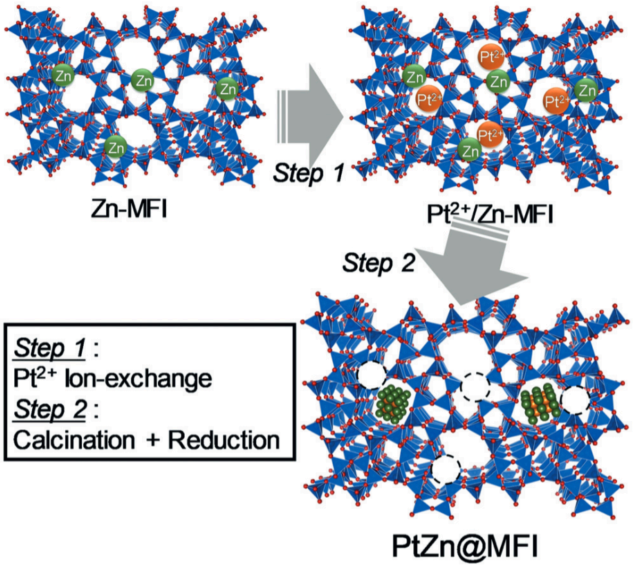

Figure 6. Overall schematic of the synthesis route for PtZn@MFI [11]

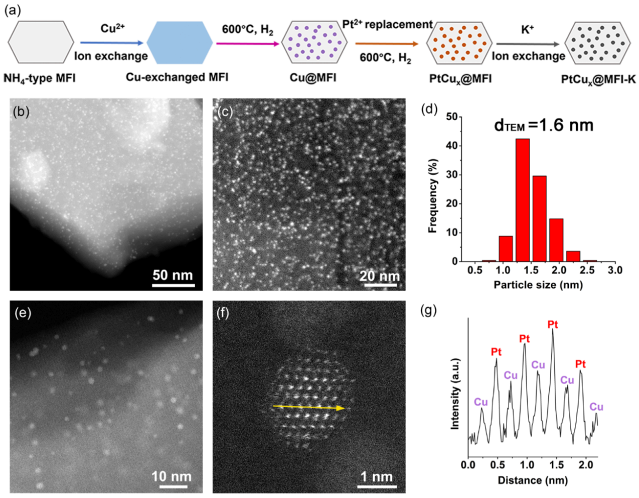

Figure 7. Schematic illustration of the synthesis process of PtCu$_x$@MFI-K catalysts [12]

Yu et al. [12] proposed a post-treatment strategy based on ion exchange combined with displacement reaction: using commercial zeolites as carriers, Cu^{2+} was first exchanged into the zeolite crystals and then reduced, and then Cu was used as the sacrificial metal to replace the subsequently introduced [Pt(NH$_3$)$_4$](NO$_3$)$_2$ (Figure 7); In addition, Cu can act as an additive to facilitate the dispersion of Pt atoms, thereby enhancing the catalytic performance of Pt. Based on this strategy, this study successfully encapsulated the PtCu alloy species (PtCu@MFI) in the ZSM-5 (MFI structure) zeolite, effectively adjusting the Pt/Cu ratio by regulating the silicon-aluminum ratio and metal loading of the ZSM-5 zeolite. The PtCu$_5$@MFI-K sample (molar Pt/Cu = 1/5) showed excellent performance in the propane dehydrogenation reaction, with a propane conversion rate of 49.7% and a propylene selectivity of over 90% at 550°C and a heavy time-space velocity (WHSV) of 3.6 h^{-1} (Figure 8). In addition, the catalyst demonstrated good cycling stability, further demonstrating its potential for application in the propane dehydrogenation reaction.

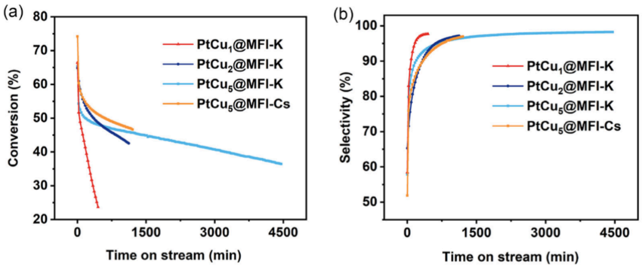

Figure 8. (a) Propane conversion and (b) propyleneselectivity over PtCu$_1$@MFI-K, PtCu$_2$@MFI-K, PtCu$_5$@MFI-K, and PtCu$_5$@MFI-Cs. Reaction condition: WHSV = 3.6 h^{-1}, 550ºC [12]

3.2. One-pot synthesis method

One-pot synthesis, enabling highly controllable metal dispersion via in-situ introduction of Pt precursors during zeolite crystallization, is a promising strategy for high-performance Pt-zeolite catalysts. Typically, a hydrothermal gel system is constructed with silicon/aluminum sources, structure-directing agents (e.g., TPAOH, TEAOH), basic mineralizers, and complexed Pt precursors (e.g., Pt(NH$_3$)$_4$Cl$_2$, Pt-en, Pt-amine complexes) [13] (Figure 9).

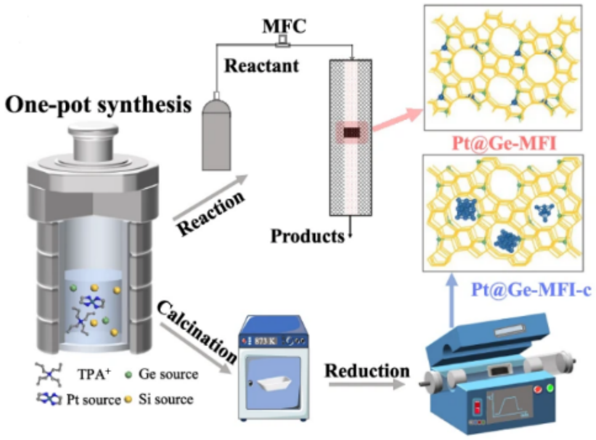

Figure 9. Scheme to show the synthesis procedures of Pt@Ge-MFI and Pt@Ge-MFI-c [13]

Regulating gel pH, complexing agents, Si/Al ratio and crystallization temperature enables uniform dispersion of Pt species as Pt^{2+} or $Pt(OH)_x$ in precursor gels at early crystallization stages (avoiding Pt hydrolysis precipitation in impregnation) [13,14]; Pt ions are anchored at zeolite framework defects or isomorphic sites to form Pt-O-T (T=Al, Fe, Ge) coordination for atomic-level confinement [13-15], and framework confinement coupled with strong metal-support interaction preserves Pt as single atoms or subnanoclusters after calcination (inhibiting agglomeration) [14], endowing catalysts like Pt/MFI, Pt/SAPO-11 and Pt/CHA with intact crystallinity and controllable interfaces [11,13]. Advanced characterizations verify these structures: XRD confirms intact zeolite topology without observable Pt diffraction peaks (Figure 10) [13]; HAADF-STEM visualizes uniform ultrafine Pt species (distinct from large particles in post-synthetic catalysts) [12,14]; XPS/XANES confirm $Pt^{2+}/Pt^{\delta+}$ species with electron coupling [16], and EXAFS reveals Pt-O coordination (negligible Pt-Pt bonding) [14]; CO-DRIFTS identifies isolated Pt sites [13]; NH_3-TPD/Pyridine-IR shows moderate Brønsted acidity (favoring Pt anchoring and propylene selectivity) [11].

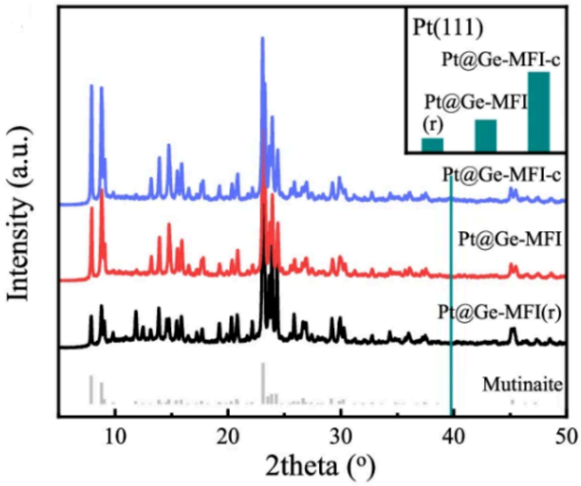

Figure 10. XRD patterns of Pt@Ge-MFI samples [13]

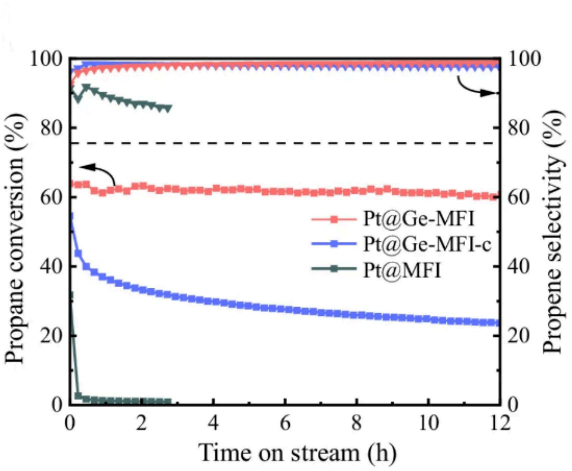

Figure 11. The catalytic performance of Pt@Ge-MFI, Pt@Ge-MFI-c, and Pt@MFI. The PDH reaction is carried out under the conditions of WHSVpropane = 1.75 h−1, propane/N2 = 1/3, 873 K and atmospheric pressure [13]

In propane dehydrogenation, one-pot synthesized Pt-zeolite catalysts outperform post-synthesis counterparts in activity, selectivity and stability shown in Figure 11. Featuring highly dispersed Pt atoms, stable Pt-O-T anchoring sites and channel confinement that mitigates sintering and coking, the catalysts deliver 35-45% propane conversion at 550-600°C, far exceeding 20-30% of impregnated samples, with propylene selectivity reaching 95-99% owing to the favored C-H activation and suppressed C-C cleavage over single-atom Pt [14,17]; typical cases include Pt_1@Ge-MFI with 98% propylene selectivity and stability over 750 h [13], and PtNP@Zn-S-1 with 51% conversion, 99.3% selectivity and stable operation for 120 h at 550°C [17], while post-synthesis catalysts deactivate rapidly within 10-20 h. The Pt-O-framework structure strengthens metal-support interaction to stabilize Pt atoms and inhibit side reactions [14,15], and zeolite confinement optimizes mass transfer for improved performance, making one-pot synthesis a promising industrial strategy for fabricating sintering-resistant single-atom Pt catalysts [13-17].

4. Conclusion

In conclusion, zeolite-supported Pt-based catalytic systems represent the core materials with superior comprehensive performance and immense application potential for propane direct dehydrogenation. The Horiuti-Polanyi stepwise dehydrogenation mechanism unravels the rate-determining feature of C-H bond activation, as well as the regulatory effects of surface sites and alloy coordination on primary and side reactions, laying the theoretical foundation for the targeted optimization of catalysts. In contrast to conventional post-synthetic strategies including impregnation and ion exchange, one-pot in situ crystallization enables atomic-level dispersion and framework anchoring of Pt species, and constructs robust interfacial synergistic structures, exhibiting remarkable merits in enhancing catalytic selectivity and high-temperature long-term stability. Future investigations will leverage in situ characterization techniques and theoretical calculations to gain in-depth insights into the dynamic structure-activity relationship. Furthermore, efforts will be devoted to breaking through efficient, low-cost and scalable in situ synthesis routes, integrating heteroatom doping and hierarchical pore engineering to develop multifunctional support systems, thus facilitating the industrialization and widespread application of highly stable and low-consumption Pt-based PDH catalysts.

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