

Research progress on supports for Rh-based catalysts in heterogeneous hydroformylation of olefins

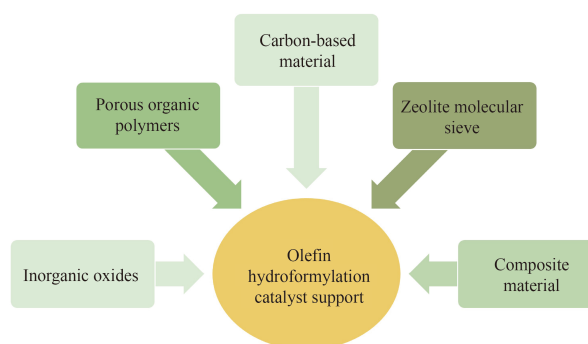
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Abstract: Olefin hydroformylation, as a key process for synthesizing high-value-added aldehydes, has extended its application scope from short-chain olefins to long-chain olefins (C₆₊). Traditional homogeneous catalytic systems face challenges such as difficulty in separating and recovering precious metal rhodium (Rh), making heterogeneous catalytic systems for olefin hydroformylation a research hotspot. By designing catalyst supports, these issues can be effectively addressed. This review summarizes recent research progress in supports for heterogeneous Rh-based catalysts, with a focus on the influence of the structural regulation strategy of the inorganic oxide-supported catalysts, porous carbon-supported catalysts, organic porous polymer-based catalysts, zeolite-supported catalysts, and composite-supported catalysts on the dispersion of active sites, regioselectivity and the cycle stability, and the review aims to provide valuable insights for the rational design of high-performance heterogeneous hydroformylation catalysts.

Key words: hydroformylation; heterogeneous catalysis; support design; long-chain olefins; aldehydes



1 Research progress in heterogeneous hydroformylation catalysts

Hydroformylation of olefins is a transition metal-catalyzed reaction that converts olefins and syngas (a mixture of CO and H₂) into aldehydes possessing one additional carbon atom under controlled temperature and pressure. As a cornerstone technology for aldehyde production^[1], it also serves as a key intermediate step in the synthesis of alcohols, carboxylic acids, and amine derivatives. The resulting C₃–C₁₈ aliphatic aldehydes are widely utilized in fragrances, pharmaceuticals, and functional materials (Figure 1(a))^[2–6]. While ethylene hydroformylation exclusively yields propionaldehyde, whereas for other α -olefins (carbon number ≥ 3), both linear and branched aldehyde isomers are produced. Owing to the higher market demand and greater value of linear aldehydes, enhancing regioselectivity—commonly expressed as the linear-to-branched (n/i or l/b) ratio—has

been established as a one of the central objective in catalyst development^[7].

The hydroformylation reaction has evolved from cobalt-based catalytic systems to rhodium-based ones, as well as from homogeneous to heterogeneous catalytic processes (Figure 1(b)). The olefin hydroformylation reaction was first discovered by German chemist Otto Roelen in 1938^[8], marking a breakthrough in metal-coordinated catalysis for C–C bond formation, which overcame the limitations of traditional aldehyde synthesis *via* alcohol dehydrogenation^[9]. In 1942, Germany constructed the world's first industrial-scale hydroformylation plant with an annual capacity of over 10000 tons^[10], signifying the initiation of its industrial application. Today, hydroformylation has developed into a crucial chemical process with an annual production exceeding 10 million tons and an output value surpassing US\$100 billion^[11].

Early hydroformylation reactions employed cobalt-based catalysts. Although cost-effective, these systems required

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severe operating conditions (20–30 MPa, 150–200 °C), hence termed the “high-pressure cobalt process”, and exhibited relatively low catalytic activity and stability^[12]. With advances in coordination chemistry, the introduction of tertiary phosphine ligands into the cobalt carbonyl system, significantly enhanced reactivity and reducing the operating conditions to milder conditions (5–10 MPa, 160–180 °C). However, this modification was prone to promoting hydrogenation side reactions. In 1960, rhodium (Rh) catalysts with superior catalytic performance began replacing cobalt catalysts. Rh is characterized by high coordination ability, allowing hydroformylation to proceed under considerably milder conditions (80–120 °C, 1–5 MPa). The further addition of triphenylphosphine (PPh₃) as a ligand markedly enhanced both catalytic activity and regioselectivity (n/i ratio) toward linear aldehydes^[13–14]. Consequently, research focus shifted to rhodium-based systems. In 1970, companies such as Ruhrchemie in Germany and Union Carbide Corporation (UCC) in the United States established industrial-scale hydroformylation plants using homogeneous Rh catalysts^[15]. Operating at 85–130 °C and 1.8–6 MPa, this approach became known as the “low-pressure oxo (LPO) process”. Nevertheless, the LPO process faces challenges, including the high cost of the noble metal rhodium (approximately 50 times more expensive than cobalt), the requirement for substantial amounts of phosphine ligands, and difficulties associated with rhodium recovery^[16–17].

In response to the challenge of rhodium recovery, Wiebus et al.^[18] pioneered in 1980 an aqueous/organic biphasic catalytic process (RCH/RP process) by developing a water-soluble rhodium-phosphine complex catalyst system. This innovation enabled the recycling of homogeneous complex catalysts, representing a significant breakthrough in the field. However, for higher olefins (carbon number ≥ 6), the resulting products exhibit high boiling points (>200 °C), necessitating separation *via* high-temperature distillation. Under such conditions, rhodium catalysts are prone to thermal decomposition and deactivation, accompanied by high energy consumption. In contrast, cobalt catalysts, owing to their superior thermal stability and ease of recovery, continue to dominate the hydroformylation processes for higher olefins^[19].

Although cobalt-based catalysts dominate the industrial hydroformylation process of higher olefins owing to their exceptional thermal stability and facile recyclability, their catalytic activity and regioselectivity are generally significantly inferior to those of rhodium-based homogeneous catalysts, making efficient and selective synthesis of higher aldehydes challenging. Compared with homogeneous systems, heterogeneous catalysts offer distinct advantages in terms of ease of separation and reusability. However, conventional supported heterogeneous catalysts often encounter dual challenges of insufficient activity and selectivity in higher olefin reactions, primarily due to inadequate exposure of active sites and difficulties in precisely modulating the

coordination environment^[20–22]. Consequently, developing novel catalytic systems that integrate the high activity of homogeneous catalysis with the recyclability of heterogeneous catalysis has become a crucial research direction for overcoming the technical limitations in the hydroformylation of higher olefins.

In recent years, the emergence of single-atom catalysis (SAC) has opened up new avenues for the heterogenization of hydroformylation catalysts. The concept of SAC was first proposed by Academician Zhang Tao in 2011, which achieves atomic dispersion and near-100% metal utilization by anchoring isolated metal atoms onto support surfaces^[23–24]. A growing body of research has been conducted on single-atom catalysis, further substantiating its potential to replace homogeneous catalysts^[25–29]. Yuan et al.^[30] developed a porous organic polymer-supported single-atom Rh catalyst (Rh1/POPs), which achieved 98% conversion and excellent stability in ethylene hydroformylation. In 2022, the Dalian Institute of Chemical Physics, Chinese Academy of Sciences, in collaboration with Zhejiang Ningbo Juhua New Materials Co., Ltd., successfully commissioned the world's first industrial-scale demonstration plant with an annual capacity of 50000 tons using single-atom Rh catalysts. This milestone addressed the long-standing challenge of ligand leaching in the heterogenization of homogeneous catalysts and marked the transition of SAC technology from laboratory research to industrial implementation.

Current research has been predominantly focused on strategies for the heterogeneous immobilization of homogeneous catalysts with high activity, superior regioselectivity, and enhanced stability, as highlighted in several recent reviews^[31–35]. Although numerous reviews on heterogeneous hydroformylation systems have been published, the majority have centered on metal centers or ligand design, while systematic evaluations focusing on catalyst supports remain notably scarce. Existing literature often treats supports as inert structural scaffolds, lacking in-depth analysis of the the structure-activity relationships between support properties (e.g., pore confinement, surface functional groups) and catalytic performance. Furthermore, cross-category comparisons among different classes of support materials and rational design principles remain underdeveloped^[20,36–37]. To address this gap, the present review focuses specifically on the pivotal role of supports in Rh-based heterogeneous hydroformylation catalysts, systematically categorizing modulation strategies involving inorganic oxides, carbon materials, porous organic polymers, zeolites and composite supports. Centered on the core logic of “support structure- microenvironment of active centers-catalytic performance”, this review delves into the functional mechanisms of supports in stabilizing metallic species, modulating selectivity, and facilitating mass transfer. In comparison with existing reviews, this work offers a more systematic and forward-looking perspective, bridging a critical gap in the literature on support-oriented catalyst design, and providing a valuable reference for the rational construction of heterogeneous catalytic systems.

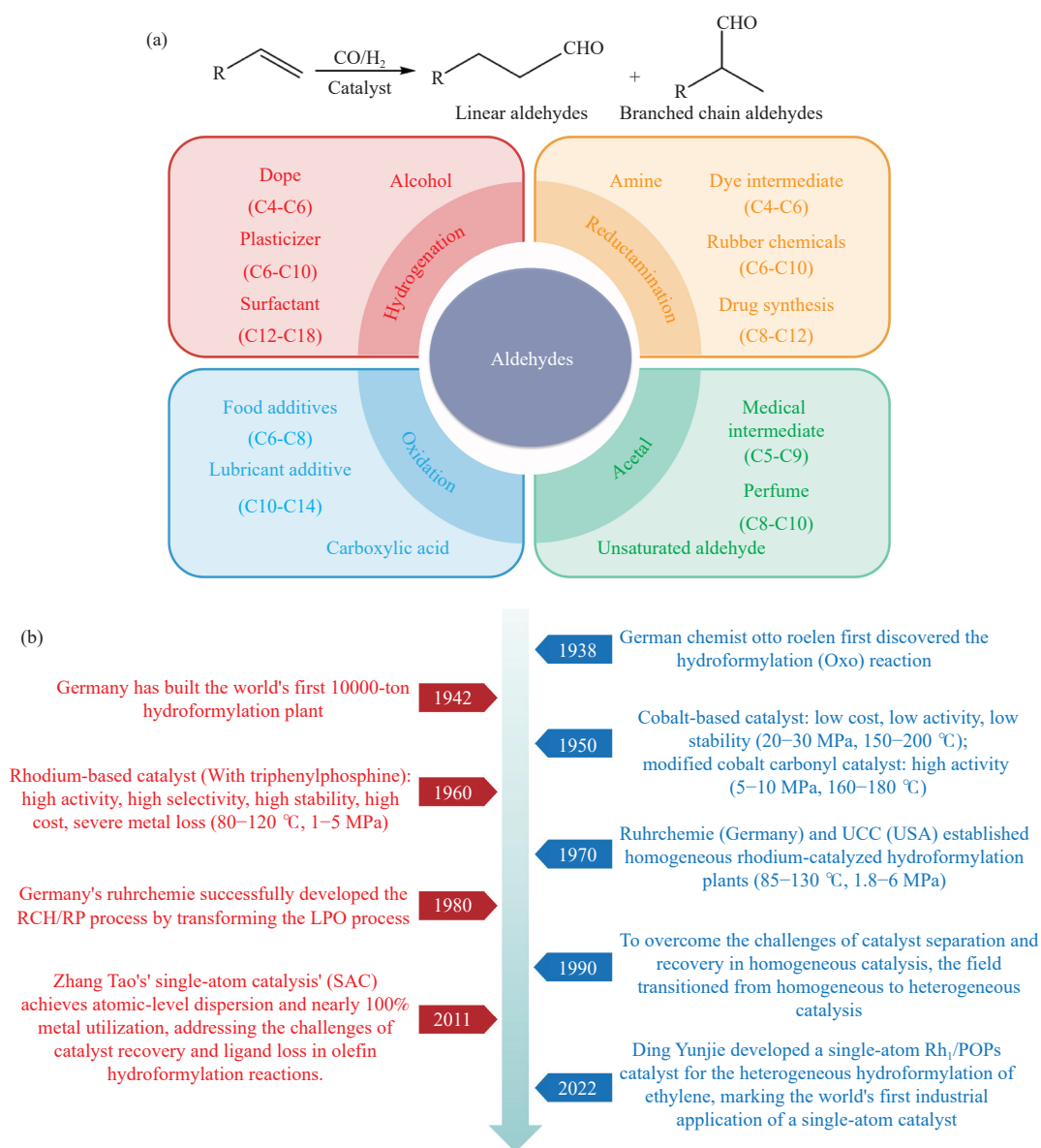


Fig. 1 (a) Olefin hydroformylation mechanism, application^[1–2,4,6,38–40] and (b) development timeline^[8–18,20,37,41–43]

1.1 Inorganic oxide-supported catalysts

Silicon oxide (SiO₂), as the most representative inorganic oxide support, has been widely employed as an ideal support for hydroformylation catalysts due to its high specific surface area (>500 m²/g), excellent chemical inertness, abundant surface hydroxyl groups, and its ability to facilitate high dispersion of metal active sites^[37]. The pore structure of SiO₂ supports significantly influences catalytic performance in hydroformylation. A macroporous structure not only optimizes mass transfer but also enhances catalytic activity and regioselectivity by modulating the electronic state of metal active centers. Liu et al.^[44] compared the performance of Co catalysts supported on macroporous (pore size: 83.7 nm) and mesoporous SiO₂. Although the cobalt nanoparticles sizes were approximately (~3.42 nm), the macroporous Co/SiO₂ catalyst yielded 11 times higher heptanal production in 1-hexene hydroformylation (130 °C, 5 MPa) than its mesoporous counterpart. The macroporous

catalyst achieved a 1-hexene conversion of 50.87% with an n/i ratio of 2.38, compared to only 28.34% conversion for the mesoporous catalyst. This is attributed to the macroporous structure effectively reducing diffusion resistance of reactants and products within the pore channels, thereby facilitating more efficient formation and conversion of active intermediates. XPS analysis confirmed that the electronic state of Co species on the macroporous SiO₂ support is more favorable for linear CO adsorption, promoting the CO insertion step in the hydroformylation reaction.

Compared to Co catalysts, Rh catalysts significantly enhance reaction activity but suffer from poor regioselectivity. Ligand modification is a key strategy to overcome selectivity limitations^[13–14]. Han et al.^[45] prepared an Rh/SiO₂ catalyst using 9.7 nm mesoporous SiO₂, which achieved 99% styrene conversion at 60 °C and 5 MPa. The enhanced activity is attributed to the stronger ability of Rh sites to activate CO and H₂ and the formed Rh-H species

facilitating hydrogen insertion (Figure 2(a)). However, the n/i ratio of Rh/SiO₂ was 2.03, comparable to that of the Co/SiO₂, indicating that merely changing the active metal does not resolve the regioselectivity issue. Zhu et al.^[46] modified Rh/SiO₂ with triphenylphosphine (PPh₃) ligands for 1-hexene hydroformylation, increasing the n/i ratio to 3.1, significantly higher than the unmodified catalyst (n/i ratio = 1.9). The study revealed that organophosphine ligands enhance catalytic performance through three synergistic mechanisms: (1) The lone pair electrons of P donate electron density to the Rh center, downshifting the *d*-band center by 0.35 eV, optimizing the adsorption strength of CO and H₂, and reducing the CO insertion energy barrier from 82.5 to 74.3 kJ/mol; (2) PPh₃ provides steric hindrance around Rh, favoring a specific orientation for 1-hexene approach, with DFT calculations confirming the linear addition transition state is 12.3 kJ/mol lower in energy than the branched addition pathway; (3) The hydrogen-bonding between the ligand and surface hydroxyls of SiO₂ creates a dynamically stable microenvironment, maintaining Rh species in a single-dispersed state and enabling stable operation for over 1000 h without Rh leaching. However, this catalyst achieved only 23.1% conversion of 1-hexene, likely due to hindered diffusion of 1-hexene molecules caused by the bulky phosphine ligand structure, which reduces accessibility to active sites.

Therefore, precise matching between the pore channels of the support and the steric hindrance of the ligands is essential to address the imbalance between reactivity and regioselectivity. Yan et al.^[47] investigated the effect of pore size in the ordered mesoporous silica SBA-15 on the hydroformylation performance of propylene. They found that the pore size of Rh-loaded SBA-15 (2.2, 3.8, 6.1 and 8.7 nm) significantly influenced the reaction. The catalyst with a pore size of 6.1 nm exhibited optimal performance in propylene hydroformylation (120 °C, 1.0 MPa), achieving an n/i ratio of 12.7 and a TOF of 245 h⁻¹. In comparison, the catalyst with 3.8 nm pores showed an n/i ratio of 11.8 and a TOF of 225 h⁻¹, while the one with 2.2 nm pores exhibited a reduced n/i ratio of 9.9 and a TOF of 119 h⁻¹. The catalyst with 8.7 nm pores demonstrated an n/i ratio of 11.0 and a TOF of 202 h⁻¹. This indicates that an optimal pore size facilitates the formation of the HRh(CO)₂(PPh₃)₂ active species and provides sufficient confinement to promote the linear intermediate formation. Although the SBA-15 support effectively immobilized Rh species *via* Rh–O and Rh–Rh bonds, maintaining catalytic activity even after 100 h of operation, the loss of phosphine ligands (approximately 18.7%) led to insufficient long-term stability of the catalyst. In contrast, Liu et al.^[48–49] attempted to optimize steric hindrance by varying alkyl chain length of phosphine ligands but struggled to simultaneously achieve high activity and regioselectivity (TOF < 50 h⁻¹). Notably, phosphine ligands are prone to oxidative deactivation under high-temperature reaction conditions, and the thermal stability of phosphine-containing catalysts remains an unresolved challenge. Kardasheva et al.^[50] fabricated a highly active Rh-UFSi catalyst by supporting Rh on

nitrogen-doped SiO₂, where nitrogen atoms were successfully incorporated into the silica framework to form Si–N bonds. This facilitated the high dispersion of Rh in a single-atom state and resulted in a decrease of 0.8 eV in the Rh 3*d*_{5/2} binding energy, thereby increasing the electron density at the Rh center. In the hydroformylation of 1-octene under the conditions of 140 °C and 5.0 MPa, the catalyst achieved complete conversion and a high turnover frequency (TOF) of 9900 h⁻¹. This high performance is ascribed to the electron donation from the lone pair on nitrogen to the Rh center, which reduces the CO adsorption energy and thus facilitates the CO insertion step. Moreover, the Si–N bonds also enhanced Rh-support interaction, suppressing Rh migration and agglomeration. Furthermore, N-doping increased support hydrophobicity, favoring olefin adsorption and enrichment. After 10 reaction cycles, the catalyst maintained >95% of its initial activity, outperforming phosphine-modified catalysts, but its n/i ratio was only 0.51, significantly lower than that of phosphine-modified systems. This is attributed to the promoting effect of nitrogen doping on CO adsorption at the expense of olefin adsorption, as well as alterations in the olefin adsorption orientation, which lowered the formation energy of the branched alkyl intermediate by 8.2 kJ/mol relative to the linear counterpart. These results indicate that while modulating the coordination environment of the active center *via* support doping can mitigate ligand leaching, its ability to regulate regioselectivity remains relatively limited.

Currently, monometallic Rh catalysts supported on pure SiO₂ struggle to balance reactivity, regioselectivity and stability. Bimetallic synergistic strategies can create superior active site microenvironments through the interplay of electronic and geometric effects between metals, thereby enhancing catalytic reactivity.^[51–53] Huang et al.^[54] prepared a Co-Rh bimetallic catalyst (Rh-Co/SiO₂), where Co promoted Rh dispersion and optimized CO adsorption strength, increasing the TOF for ethylene hydroformylation from 2511 to 2790 h⁻¹ and improving chemoselectivity from 43% to 52%. The study showed that Co addition significantly increased CO adsorption (from 1.04 to 1.68 μmol/g), with moderate CO adsorption strength facilitating the migration and insertion into adsorbed ethyl species and suppressing hydrogenation side reactions (Figure 2(b)). Although regioselectivity is not a concern for ethylene, the synergistic mechanism provides a foundation for addressing challenges with higher olefins. A notable drawback is the high reaction temperature required (180 °C), leading to substantial energy consumption. Beyond silicon dioxide (SiO₂) supports, inorganic oxides possessing unique electron transfer capabilities, surface oxygen vacancies, and acid sites are also important catalyst supports^[1,55–56]. For instance, high-surface-area nano-oxides can enhance metal dispersion and utilization efficiency, while precise design of surface oxygen vacancies can modulate the adsorption and conversion pathways of reaction intermediates, significantly boosting activity and selectivity. Jagtap et al.^[57] prepared a high-loading Rh/Cu₂O nano-catalyst (8.5% Rh) that

achieved 99% conversion in 1-hexene hydroformylation (90 °C, 3.5 MPa). This high performance is attributed to interfacial electron transfer from Cu^+ sites to Rh, increasing Rh electron density, enhancing CO adsorption strength, and promoting CO insertion into alkyl intermediates. Moreover, the strong interaction between the Cu_2O support and Rh also improved resistance to leaching, maintaining over 92% conversion after 4 catalytic cycles. Additionally, increasing reaction pressure also favored CO adsorption and thus conversion, but enhanced CO adsorption promoted branched aldehyde formation, reducing regioselectivity. Surface acidity also influences hydroformylation. For example, Kontkanen et al.^[58] studied a nano-ZnO supported Rh catalyst (0.83% Rh/nano-ZnO), which achieved 100% 1-hexene conversion, but the weak acid sites on the ZnO surface facilitate the adsorption and stabilization of branched alkyl intermediates, resulting in a low n/i ratio of 0.8. Modulating the electronic and spatial environment of active centers through Strong Metal-Support Interactions (SMSI) can also enhance the performance of hydroformylation reactions^[20]. Wang et al.^[59] prepared a low-loading 0.2% Rh/CoO single-atom catalyst *via* an impregnation method, achieving high propylene conversion (94.6%) and high regioselectivity (n/i ratio = 16.9) in the hydroformylation of propylene (100 °C, 3.2 MPa). The catalytic activity remained as high as 90% after five reaction cycles (Figure 2(c)). This is attributed to the electron donation from CoO to Rh under SMSI, resulting in

an electron-rich Rh active center that weakens the adsorption strength of hydrogen species, thereby suppressing over-hydrogenation of propylene to propane. Simultaneously, the SMSI-induced CoO_x overlayer encapsulates Rh single atoms, enabling propylene to adsorb in a planar configuration that preferentially activates the terminal carbon of the double bond, leading to selective formation of linear aldehydes. Liu et al.^[60] compared Rh single-atom catalysts on CeO_2 with different morphologies (cubic, polyhedral, and rod-like) exposing (100), (111) and (110) facets, respectively. The rod-like Rh_1/CeO_2 -Rod catalyst exposing (110) facets (Figure 2(d)) exhibited best in styrene hydroformylation, with a TOF of 9386 h^{-1} . XPS showed this rod-like CeO_2 had the lowest number of surface oxygen vacancies, but the $\text{CeO}_2(110)$ facet facilitated the embedding of single Rh atoms, generating local strain and dangling bond oxygen atoms, forming a unique Rh-C-O-Ce active configuration. In this structure, Ce^{3+} sites activate CO, while Rh sites activate olefins and hydrogen, and their synergistic interaction significantly reduces the reaction activation energy. Additionally, the energy barrier for linear aldehyde formation on Rh_1/CeO_2 -Rod was 12.8 kJ/mol lower than that for the branched aldehyde, enhancing regioselectivity (n/i ratio = 3.2) and outperforming other morphologies. This catalyst also maintained stable activity over 5 cycles, although the precise control required for rod-shaped CeO_2 poses challenges for industrial application.

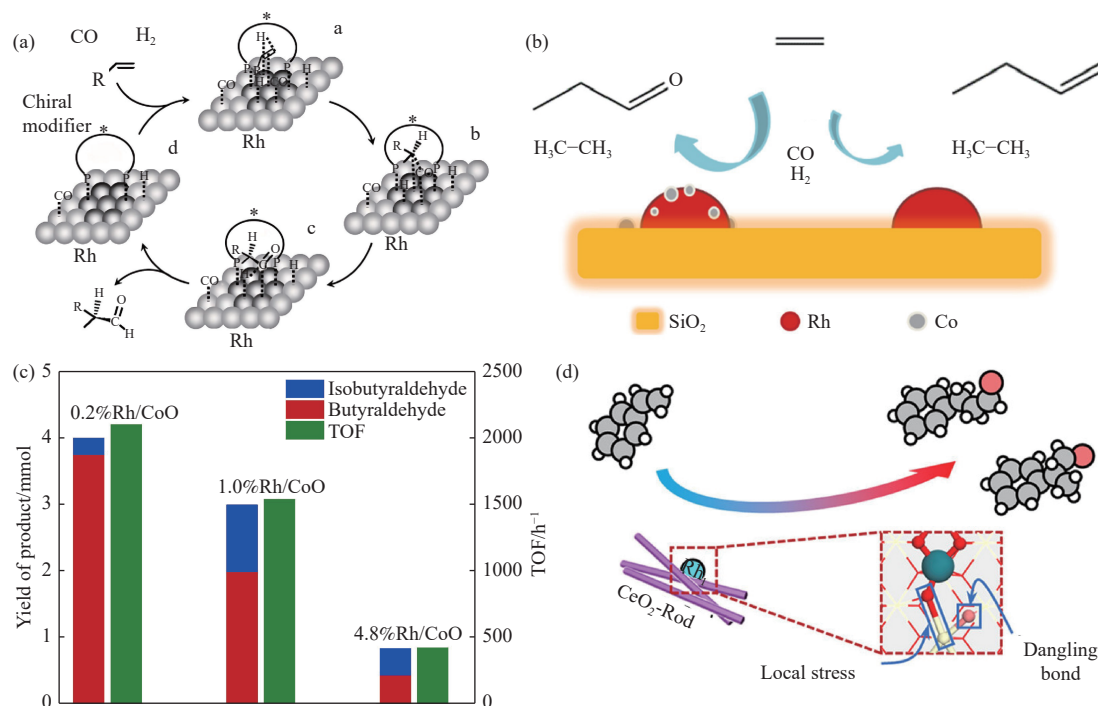


Fig. 2 (a) Schematic of the reaction pathway for hydroformylation over Rh/SiO₂ catalyst^[45]; (b) Schematic of ethylene hydroformylation catalyzed by Rh-Co/SiO₂ bimetallic catalyst^[54]; (c) Results of propylene hydroformylation over Rh/CoO with different loadings (0.2%, 1.0%, 4.8%) at 100 °C^[59]; (d) Mechanism of the morphology effect of Rh₁/CeO₂ catalyst on styrene hydroformylation^[60]
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1.2 Porous carbon-supported catalysts

Carbon-based materials with porous structure and high specific surface areas (typically 500–1500 m²/g) enable high dispersion of the metal active components, thereby suppressing the deactivation caused by metal particle agglomeration^[61–62]. More importantly, the abundant edge/corner sites on the carbon materials can promote linear adsorption and activation of CO, which is favorable for the insertion reaction of the C=C bond. Zhang et al.^[63] prepared an activated carbon-supported Rh/AC catalyst, which achieved a 99.6% conversion in 1-hexene hydroformylation, but with low regioselectivity (n/i ratio = 0.6). This phenomenon is attributed to the high CO coverage on Rh sites under high-pressure conditions, where increased steric hindrance leads to preferential adsorption of the alkene at the α -carbon, thereby favoring CO insertion at the β -carbon (Figure 3(a)). Although high-surface-area activated carbon provides adequate sites for Rh dispersion, its limited tunability of surface electronic properties poses constraints. Surface functionalization of carbon materials can tune the electronic environment of the active sites, offering a solution to the imbalance between activity and selectivity. Tan et al.^[64] prepared a reduced graphene oxide (RGO)-supported Rh/RGO catalyst *via* a “one-pot” method. The two-dimensional nanosheet structure and abundant surface functional groups of RGO enhanced metal dispersion. The higher exposed surface area of Rh sites (1.60 m²/g) and dispersion (18.12%), improved the accessibility of the active sites, leading to superior performance (100% conversion, n/i ratio = 4.0) under mild conditions (70 °C, 5 MPa) in the hydroformylation of 1-hexene, significantly outperforming Rh/AC (n/i ratio = 0.8) and Rh/CNTs (n/i ratio = 2.8) catalysts. Recognizing the critical role of surface functional groups on carbon supports, Tan et al.^[65] further treated Rh/AC with nitric acid oxidation to introduce more oxygen-containing functional groups (e.g., carboxyl or carbonyl). These oxygen-containing groups, likely situated near Rh sites, may conjugate with the α -carbon of 1-hexene adsorbed on Rh. Acting as electron-withdrawing moieties, they increase the negative charge density on the α -carbon *via* an inductive effect. Under such conditions, the intermediate formed by α -C hydrogenation becomes unstable, prompting Rh to favor hydrogen addition to the β -carbon of the 1-alkene, thereby favoring linear aldehyde formation and enhancing regioselectivity (n/i ratio = 2.3) (Figure 3(b)). However, the improvement in catalytic performance achieved solely by introducing oxygen-containing groups *via* surface functionalization remains limited, and these groups exhibit poor thermal stability under reaction conditions. Li et al.^[66] prepared a pure silica silicalite-1 membrane-coated Rh/activated carbon core-shell catalyst (S1/Rh/AC) *via* a hydrothermal method for 1-hexene hydroformylation. The regioselectivity (n/i ratio = 2.3) was significantly higher than that of the uncoated catalyst (n/i ratio = 0.5), while maintaining a high conversion (~96%). This enhancement is attributed to the pore size of the silicalite-1 membrane (0.56 nm $\times$ 0.54 nm)

is similar to the kinetic diameters of linear and branched aldehydes. The pore confinement effect caused a significantly higher diffusion rate of *n*-heptanal within the micropores compared to iso-heptanal. The differential diffusion rates increase the surface concentration of the linear aldehyde and suppress the formation of the branched product, thereby improving regioselectivity. Similar to phosphorus-modified inorganic oxide supports, anchoring specific organic phosphine ligands on carbon supports can also enhance the regioselectivity^[67–68]. Tan et al.^[67] prepared a PPh₃-modified PPh₃-Rh/RGO catalyst *via* a one-pot method. During synthesis, PPh₃ acted as a reducing agent, removing oxygen-containing groups from graphene oxide (GO) to form defective RGO, thereby improving Rh dispersion (increasing from 14.16% to 18.23%). Simultaneously, PPh₃-Rh active species were formed. PPh₃ donates electrons to the Rh sites, optimizing CO adsorption strength and promoting CO insertion. Meanwhile, the PPh₃ ligands create steric hindrance around Rh sites, causing 1-hexene to preferentially adsorb *via* the terminal carbon onto the Rh sites, thus promoting *n*-heptanal formation. DFT calculations indicated that the formation energy of linear alkyl intermediate was 8.7 kJ/mol lower than that of the branched isomer, increasing the n/i ratio from 0.90 (without PPh₃) to 2.1. The catalyst achieved a high 1-hexene conversion of 99.9% (at 90 °C and 5 MPa). However, it exhibited poor thermal stability, decomposing at 250 °C. Yang et al.^[69] prepared a PPh₃-RhAC-SA/N-C catalyst *via* an adsorption-pyrolysis-phosphorylation method. This catalyst featured a dual-active sites comprising Rh-N₄ single-atom and Rh cluster. The strong coordination bond between the N-containing carbon and Rh (Rh-N₄) conferred high thermal stability. Moreover, the synergistic effect between the Rh clusters and PPh₃-Rh-N₄ increased the Rh-P bond dissociation energy from 2.1 to 2.7 eV, significantly enhancing the stability of phosphine ligand. The catalyst exhibited excellent performance in 1-hexene hydroformylation (100 °C, 4.0 MPa) with a TOF of 6599 h⁻¹, 96% conversion, and n/i ratio = 2.57. Its activity remained stable after 5 reaction cycles, outperforming conventional Rh-PPh₃ catalysts. However, the synthesis process involves multiple complex steps and is challenging to scale up. Wei et al.^[70] prepared a carbon-nanotube encapsulated Co@N-CNTs/RhP catalyst *via* an impregnation method, which demonstrated ultra-high activity (TOF up to 82603 h⁻¹) and high remarkable cycling stability (no degradation over 25 cycles) (Figure 3(c)) in 1-hexene hydroformylation. This performance is attributed to the specific structural design of the N-doped carbon nanotubes (N-CNTs) and RhP sub-nanoclusters: nitrogen atoms in the N-CNTs form strong Rh-N bonds with RhP, facilitating electron transfer from N to Rh active sites. Such strong coordination effectively anchors Rh atoms and enhances their catalytic activity. Meanwhile, Co nanoparticles are precisely confined within N-CNTs (diameter ~5 nm), creating a physical barrier *via* spatial confinement that inhibits the migration and aggregation of RhP sub-nanoclusters.

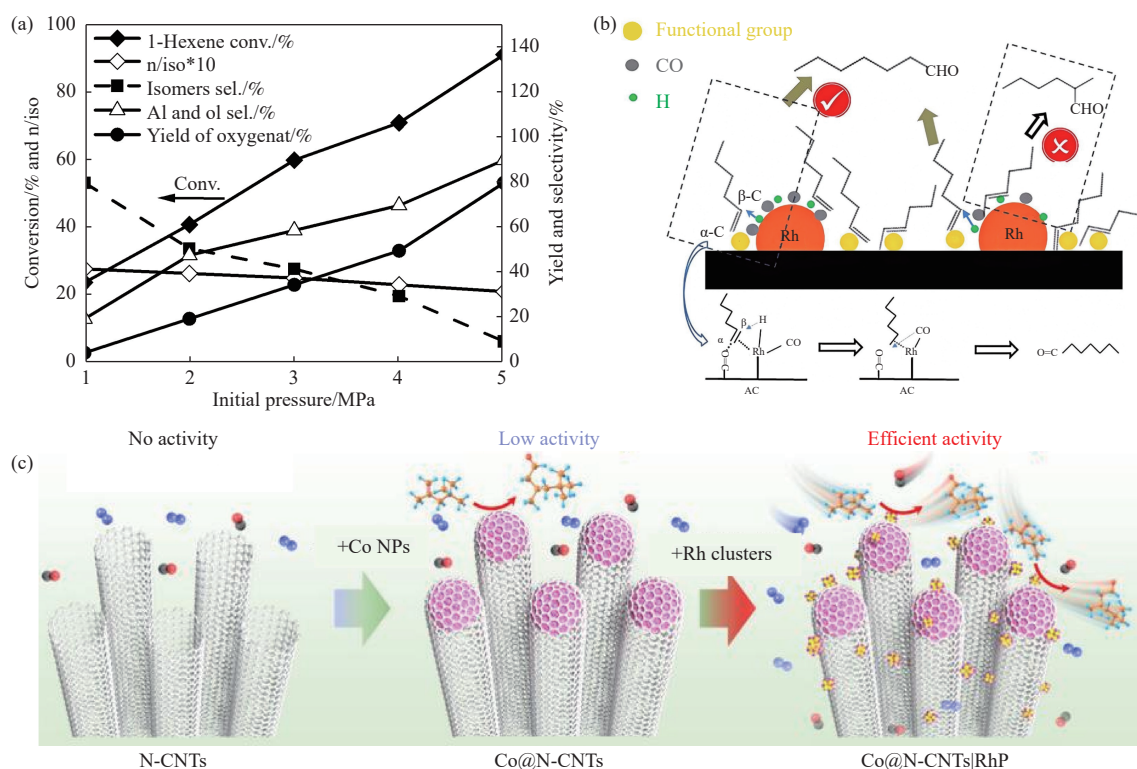


Fig. 3 (a) Effect of reaction pressure on the performance of Rh/AC-catalyzed 1-hexene hydroformylation (reaction conditions: 0.10 g catalyst, 40 mmol 1-hexene, 70 °C, 1 h)^[63]; (b) Effect of surface functional groups on the catalytic performance of Rh/AC-80^[65]; (c) Schematic of functional mechanism for N-CNTs, Co@N-CNTs, and Co@N-CNTs/RhP^[70] (with permission from Elsevier and ACS)

Most importantly, significant electronic synergy exists between RhP and Co nanoparticles. EXAFS characterization confirmed a Rh-Co coordination number of 2.8, which not only reduced the reaction activation energy to 64.6 kJ/mol but also enhanced the stability of Rh active sites. In contrast, Bucciol et al.^[71] prepared a carbon nanofiber-supported Rh/CNFs catalyst using high-temperature treatment. Although this catalyst achieved >99% conversion of 1-hexene, the Rh leaching reached 72.9% after 5 cycles. This is because high-temperature treatment significantly reduced the number of surface defects and functional groups on the CNFs, decreasing the anchoring sites and interaction strength for Rh, leading to easy migration and aggregation during the reaction. These comparative studies reveal that atomic-level precise design to enhance metal-support interactions (e.g., N, P doping) and introduce spatial confinement effects (e.g., phosphine ligands, pore confinement, physical isolation) are crucial pathways for addressing the issue of Rh leaching in catalysts, providing important guidance for designing highly stable heterogeneous hydroformylation catalysts.

1.3 Porous organic polymer-based catalysts

Organic polymers are considered ideal supports due to their structural flexibility and ease of functionalization. For instance, dendritic polyglycerols, rich in hydroxyl groups and featuring a three-dimensional network structure, are

commonly used as supports for active metals. However, such traditional polymer-supported catalysts often suffer from low activity^[72]. Ricken et al.^[73] anchored the NIXANTPHOS (4,6-bis(diphenylphosphino)benzoxazine) ligand onto hyperbranched polyglycerol (PG) via Michael addition and hexamethylene diisocyanate (HDI) addition, preparing a PG/PU-NIXANTPHOS-Rh(I) catalyst. This catalyst achieved a high n/i ratio of 30.25 and good stability in 1-octene hydroformylation. The improved selectivity is attributed to the wide bite angle formed by the large P-P distance in NIXANTPHOS ligand and the use of a long hexamethylene spacer (derived from the reaction of NIXANTPHOS with excess hexamethylene diisocyanate during synthesis), which allows more flexible coordination of the ligand to Rh centers, thereby favoring linear product formation. However, the 1-octene conversion was only 69%, due to the shielding of some active sites by the polymer support and an insufficient ligand-to-Rh ratio. Chitosan, as a natural polymer with abundant amino and hydroxyl groups, is suitable for multi-site modification^[74–75]. Makhubela et al.^[75] anchored phosphine ligands onto amino- and hydroxyl-rich chitosan, via Schiff base structure to construct a bidentate-coordinated Rh catalyst. This catalyst achieved a conversion of 75%–79% and an n/i value of 2.33 in 1-octene hydroformylation. Although it exhibited good recyclability, its activity remained limited due to the embedding of some Rh sites by the Schiff base structure, reducing Rh active site exposure, and the

confinement effect of the chitosan support increasing substrate diffusion resistance.

In recent years, porous organic polymers (POPs) have shown great advantages in olefin hydroformylation. Particularly, porous organic ligands (POLs), featuring high concentrations of heteroatom organic ligands (e.g., phosphorus, nitrogen, and oxygen donors), can serve both as supports and directly participate hydroformylation reaction as ligands for the metal sites^[76–78]. POLs combine the high specific surface area and hierarchical pore structure of POPs. More importantly, their ligands can form multi-dentate coordination environments with Rh site similar to homogeneous systems, akin to homogeneous systems. This design fundamentally mitigates the issue of active-site embedding, thereby enabling high activity and regioselectivity^[79–80]. Sun et al.^[79] successfully prepared a Rh/POL-PPh₃ catalyst *via* solvothermal polymerization of vinyl-functionalized PPh₃. The catalyst featured a hierarchical micro-mesoporous structure and high specific surface area (1086 m²/g), which could enhance mass transfer efficiency. The phosphine ligand concentration was as high as 2.94 mmol/g, far exceeding that of traditional supported catalysts. This high-density ligand environment favored the formation of multidentate Rh-PPh₃ active species, effectively suppressing the migration and aggregation of Rh during reaction. In 1-octene hydroformylation (90 °C, 2 MPa), this catalyst achieved nearly 100% conversion with no significant activity decay after 6 cycles. However, the regioselectivity was low (n/i ratio = 1.35) due to the high steric hindrance environment created by numerous PPh₃ ligands around Rh, which hindered linear coordination of 1-octene to Rh centers and favored branched intermediates. Furthermore, PPh₃ as a neutral ligand, have relatively fixed electronic effects, making it difficult to modulate Rh's *d*-orbital splitting energy, leading to reduced stability of linear alkyl intermediate. To improve selectivity, Li et al.^[81] prepared a Xantphos-doped Rh/POPs-PPh₃ catalyst *via* solvothermal synthesis, achieving 42% conversion of 1-octene, a TOF of 300–500 h^{−1}, and an n/i ratio of 9 at 100 °C and 1 MPa with stable cyclic performance. This is attributed to the strong coordination between Xantphos and Rh, forming stable single-atom Rh sites. In addition, the bulky structure of the support suppressed the formation of branched transition states through thermodynamic and kinetic control mechanism (Figure 4(a)). The synergistic effect between Xantphos and PPh₃ ligands in the catalyst framework was crucial for balancing selectivity and stability. When the Xantphos content was too low, the n/i ratio dropped to 0.82, while when the PPh₃ content was too low, the catalyst stability decreased (Rh leaching ~5.3%). Moreover, Li et al.^[82] synthesized a Rh/CPOL-bp&P catalyst *via* a solvothermal copolymerization method, where CPOL-bp&P denotes a copolymer of biphenylphosphine and PPh₃. Biphenylphosphine is a specialized bidentate phosphine ligand. This catalyst utilized PPh₃ and Biphenylphosphine bifunctional units to copolymerize, constructing a structure with hierarchical porous structure (pore size 0.7–18 nm), high specific

surface area (1201 m²/g) and pore volume (2.79 cm³/g). Under mild reaction conditions (70 °C, 0.5 MPa), the catalyst achieved a TOF of 1200 h^{−1} and n/i ratio > 24 in propylene hydroformylation, with stable operation over 1000 h in a continuous fixed-bed reactor. The outstanding performance is attributed to the single-atom dispersion of Rh, where each Rh atom on average coordinates with 2.8 P atoms-approximately equivalent to the coordination of one Rh atom simultaneously with one biphenylphosphine unit and one PPh₃ unit within the polymer framework. This stable multidentate structure formed by dual ligands, combined with high phosphorus species concentration and hierarchical pore environment, effectively suppressed Rh aggregation and enhanced catalytic activity and stability. Furthermore, the molar ratio of biphenylphosphine to PPh₃ must be precisely controlled. An excessively high biphenylphosphine ratio reduces the degree of copolymerization, specific surface area, and pore volume, whereas an insufficient biphenylphosphine content diminishes the steric hindrance effect, leading to reduced regioselectivity of the product. As mentioned in the earlier study by Wang et al.^[59], an appropriate Rh loading is essential. A lower Rh loading (i.e., a higher P/Rh ratio) favors improved catalytic activity and regioselectivity (Figure 4(b)). We also observed that while increasing pressure enhances the reaction rate, it adversely affects linear selectivity (Figure 4(c)), a point also highlighted in Zhang et al.'s work^[63]. These findings underscore the importance of optimizing reaction conditions based on specific application requirements. Wang et al.^[83] prepared a porous organic polymer catalyst, Rh/POP-PhPh₃-BP-P(OPh)₃ (where POP is porous organic polymer, PhPh₃ is 1,3,5-tris(4-vinylphenyl)benzene crosslinker, BP is bidentate phosphine ligand, and P(OPh)₃ is phosphite ligand), *via* solvothermal method and studied the effect of P(OPh)₃ concentration on 1-butene hydroformylation. Results showed that increased P(OPh)₃ concentration in the catalyst enhanced steric hindrance and CO adsorption, inhibiting olefin addition but favoring linear aldehyde formation, thereby improving regioselectivity, although diffusion limitations reduced reaction activity. Introducing the biphosphite ligand BP could further enhance steric hindrance and electron-deficient state, promoting the formation of linear metal-alkyl intermediates and CO dissociation. When the P(OPh)₃ concentration was 0.9 mmol/g, BP and P(OPh)₃ formed a synergistic microenvironment, allowing a balance between reaction activity and regioselectivity, achieving a TOF of 9590 h^{−1}, an n/i ratio as high as 60.4, and good catalytic stability. However, excessive ligand concentration reduces pore size and specific surface area, adversely affecting mass diffusion. Jia et al.^[80] prepared a Rh/POL-BPa&PPh₃ catalyst *via* copolymerization, using a copolymer of vinyl-functionalized phosphoramidite ligand (BP_a) and triphenylphosphine (PPh₃) as the support. The catalyst featured a porous structure (bimodal pore size distribution: 1.2–2.0 and 2.3–25 nm), relatively high surface area (423.6 m²/g), and pore volume (0.41 cm³/g).

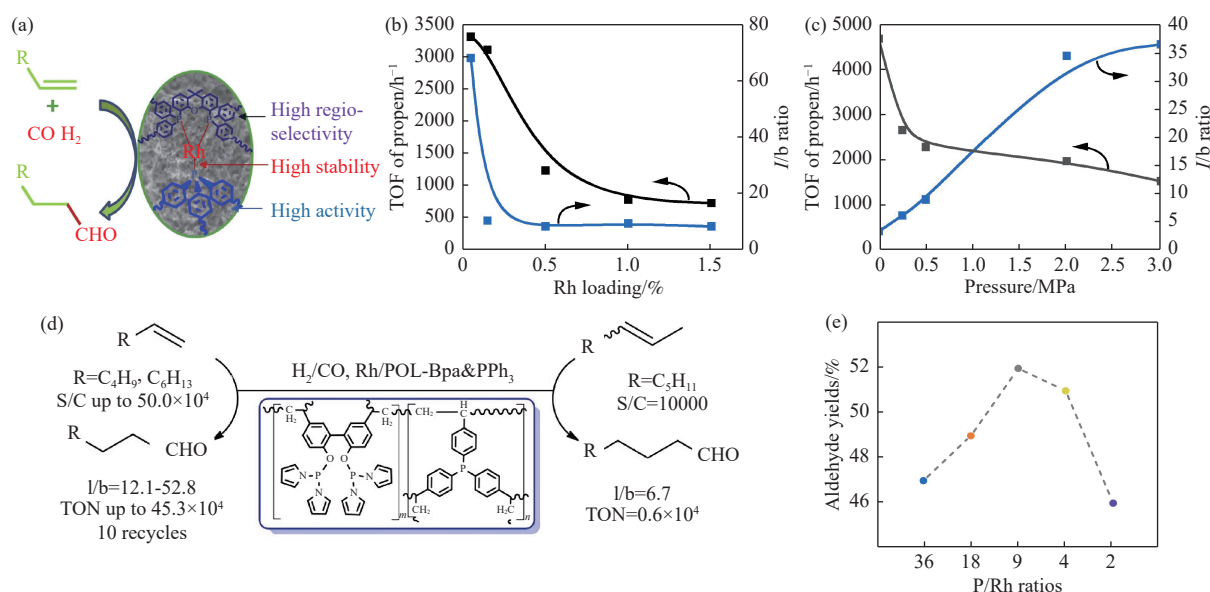


Fig. 4 (a) Schematic of ligand effect in Rh-Xantphos/POPs-PPh₃ catalyst^[81], (b) Propylene hydroformylation over Rh/CPOL1BP&10P catalyst at different Rh loadings (reaction conditions: reaction time=4 h, $p=0.5$ MPa ($C_3H_6:CO:H_2=1:1:1$), $t=70$ °C, GHSV=1500 h⁻¹)^[82], (c) Propylene hydroformylation over Rh/CPOL1BP&10P catalyst at different premixed gas pressures ($C_3H_6:CO:H_2=1:1:1$) (reaction conditions: Rh loading 0.130%, reaction time=4 h, $t=70$ °C, space velocity=1500 h⁻¹)^[82], (d) High-efficiency catalytic performance of Rh/POL-BPa&PPh₃ catalyst^[80], (e) Effect of P/Rh ratio on aldehyde yield (all tested catalysts exhibit >99.5% aldehyde selectivity and n/i ratio of 0.32; reaction conditions: 1-octene (3.0 mmol), toluene (10 mL), 100 °C, 6 h, Rh-based catalyst (0.1 mol%), $CO/H_2=1:1$ (2.0 MPa))^[84] (with permission from Elsevier, RCS and ACS)

Under conditions of 90 °C and 1 MPa, the catalyst achieved a 1-hexene conversion of 90.3%, an n/i ratio of 50.1, and a TON of 2.7×10^4 . Under higher substrate/catalyst ratio ($S/C = 50 \times 10^4$) and extended reaction time (24 h), the TON reached 45.3×10^4 . When using 2-octene as substrate under 1.0/0.5 MPa (CO/H_2), 110 °C and 15 h, the n/i ratio was 6.7 with a TON of 0.6×10^4 (Figure 4(d)). The study found that the BPa ligand unit was particularly beneficial for improving catalytic activity and regioselectivity, while the synergistic effect between PPh₃ and BPa could improve electronic modulation of Rh sites, forming sterically hindered catalytic intermediates. Furthermore, the catalyst exhibited good recyclability, maintaining high activity and selectivity after 10 cycles, with Rh leaching of only about 1.0×10^{-7} , attributed to multiple coordination of Rh by the high-density ligands in the polymer framework.

The above studies indicate that the synergistic design of biphosphine ligands can effectively enhance the regioselectivity of the product. However, strict control of phosphine ligand concentration is required to balance catalytic activity, regioselectivity, and stability. Similar to biphosphine catalytic systems, monophosphine catalytic systems also necessitate precise regulation of phosphine ligand concentration. Tang et al.^[84] prepared a Rh/phosphite-POP catalyst, where phosphite-POP was a superhydrophobic porous organic polymer synthesized by copolymerizing tris(2-tert-butyl-4-vinylphenyl) phosphite with azobisisobutyronitrile (AIBN), and found that the molar ratio of phosphite ligand to Rh (P/Rh) significantly affected the product yield and stability in 2-octene

hydroformylation (Figure 4(e)). When $P/Rh \geq 9$, the catalyst maintained stable activity and selectivity after 10 catalytic cycles with no rhodium leaching, whereas at P/Rh ratios of 4 and 2, Rh leaching reached 6.8% and 16.9% after 5 cycles, respectively. The product yield was highest at a P/Rh of 9. This phenomenon is attributed to the sufficient free ligands at high P/Rh ratios, which repair damaged active sites and suppress the leaching of Rh species.

Conventional hydroformylation processes typically employ organic solvents to enhance the solubility of CO and H₂ in the reaction system, thereby improving reaction rate^[85–86]. Recently, Wang et al.^[87] investigated the reaction performance of Rh/CPOL-BPa&1VB catalyst under solvent-free conditions. The catalyst support was a cross-linked porous organic polymer formed by copolymerization of pyrrole-based bisphosphoramidite (BPa) monomer with styrene monomer (1VB) (specific surface area: 140 m²/g, hierarchical pore size: 0.7–18 nm, pore volume: 0.4 cm³/g). This catalyst achieved 98.5% conversion of 1-hexene ($TOF = 1570$ h⁻¹) and high regioselectivity (n/i ratio = 158.5) under solvent-free conditions (80 °C, 2.0 MPa). Its excellent performance is attributed to: (a) the hierarchical pore structure efficiently adsorbed and enriched 1-hexene around the Rh sites, increasing local reactant concentration; (b) the BPa units coordinated with Rh(acac)(CO)₂ to form HRh(BPa)₂(CO) active sites, whose large cone angle steric hindrance (~145°) and strong π -acceptor character forced 1-hexene to linearly coordinate to the Rh centers, effectively suppressing branched transition state formation; (c) the hierarchical pore structure facilitated reactant diffusion and

product desorption while firmly anchoring Rh active sites through a high-density ligand environment to prevent migration and aggregation during reaction.

1.4 Zeolite-supported catalysts

Zeolites possess the high specific surface area and ordered pore structure. Supporting metal active components on zeolites can enhance metal dispersion, and the unique confinement effect of micropores enables shape-selective catalysis for reactant/product molecules, thereby improving reaction activity and regioselectivity^[41,88]. Liu et al.^[89] prepared a $\text{Rh}_2\text{O}_3@\text{S-1}$ core-shell catalyst *via* an epitaxial growth method, precisely embedding Rh_2O_3 active components within the micropores of S-1 zeolite (pore size ~ 0.55 nm). This catalyst achieved $>99\%$ conversion for both 1-hexene and 1-decene hydroformylation (80°C , 5 MPa), with n/i ratios of 1.11 and 6.65, respectively (Figure 5 (a)). The difference in regioselectivity primarily aroused from the significant molecular size difference between the linear and branched aldehyde products of 1-decene; the branched aldehyde experiences significant steric hindrance within the zeolite channels, resulting in markedly slower diffusion compared to the linear aldehyde, thus enhancing product regioselectivity. Micropores also restricted β -elimination step for double-bond isomerization of 1-decene to internal olefins, reducing branched aldehyde formation. In contrast, the heptanal isomers generated from 1-hexene

had smaller size differences, resulting in negligible differences in diffusion rates within the micropores and thus limited regioselectivity improvement. However, after 7 reaction cycles, Rh leaching was about 50% Rh, attributed to the incomplete encapsulation of Rh_2O_3 species, especially those on the external surface, significantly reducing catalytic stability. Fang et al.^[90] prepared a $\text{Rh}@\text{S-1}$ catalyst with Rh nanoparticles immobilized within silicalite-1 framework *via* hydrothermal synthesis. The Rh nanoparticles were immobilized within the zeolite framework, maintaining activity without degradation over three cycles. The highly hydrophobic Silicalite-1 selectively enriched 1-hexene, reducing competitive adsorption of water molecules at active sites and enhancing reactivity, achieving 85.8% conversion of 1-hexene, compared to only 45.4% with an impregnated catalyst. In the aforementioned pure-silica zeolites, Rh exists as nanoparticles, resulting in poor metal utilization and catalyst stability. Shang et al.^[91] prepared a Y zeolite-encapsulated isolated Rh atom catalyst ($\text{Rh}@\text{Y}$) using an *in situ* hydrothermal synthesis. The abundant framework aluminum in Y zeolite effectively dispersed and stabilized isolated Rh atoms, enhancing reaction activity and stability. This catalyst achieved a TOF of 6567 h^{-1} for 1-hexene hydroformylation at 120°C and 6 MPa, attributed to the significantly reduced activation energy (60.6 kJ/mol) of isolated Rh active sites within the zeolite framework. Compared to impregnated catalysts, it markedly improved hydroformylation activity ($106\text{ mol C/mol Rh/h}$) with no Rh leaching after 5 cycles (Figure 5(b)).

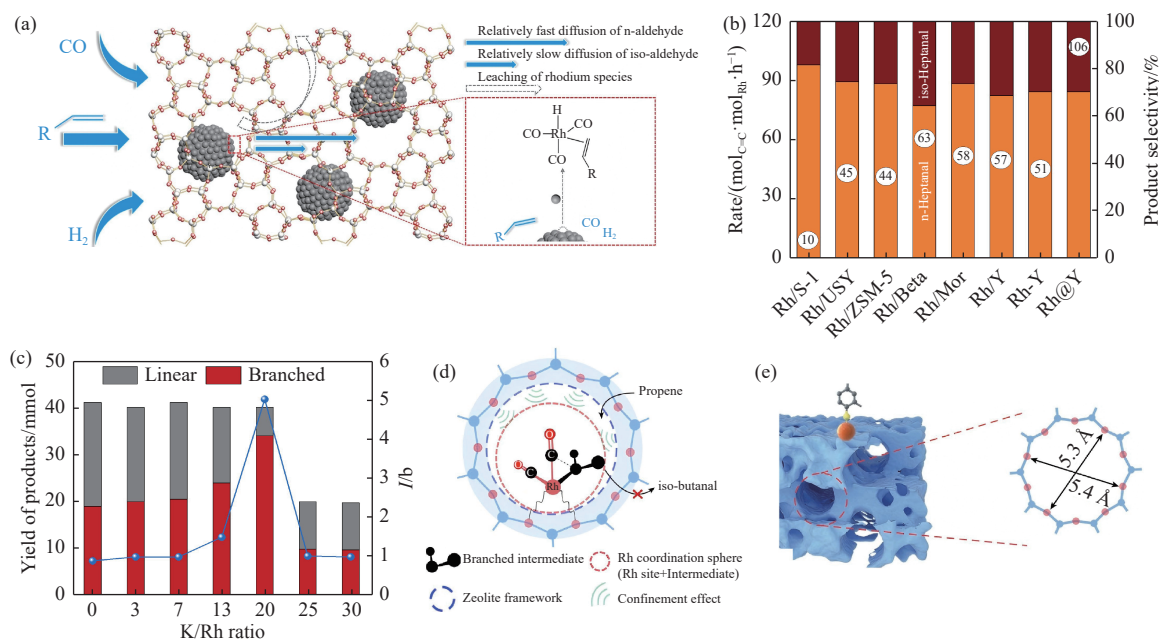


Fig. 5 (a) Schematic of hydrogenation process over rhodium oxide catalyst embedded in zeolite microchannels^[89]; (b) Comparison of catalytic performance for 1-hexene hydroformylation over various Rh-containing zeolites (reaction conditions: 0.05 g catalyst, 3 mmol 1-hexene, 1.5 mL toluene, 6 MPa CO/H₂ (1 : 1, mole ratio), 60°C , 1 h)^[91]; (c) Propylene hydroformylation catalyzed by K-Rh/S-1 catalyst (reaction conditions: 0.1 g catalyst, 0.2% Rh, propylene (0.5 MPa), CO/H₂ (1 : 1, 5 MPa), toluene (5 mL), 85°C , 3 h)^[93]; (d) Schematic illustration of confinement effect in molecular sieve catalysts^[94]; (e) Schematic illustration of the kinetic size of $\text{Rh}_{\text{OD}}@\text{MEL-DMBT}$ ^[94]

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However, its regioselectivity was low (n/i ratio = 1.28) due to the poor spatial confinement capability of Y zeolite's large pore openings (0.71 nm), where the energy barrier difference between linear and branched aldehyde formation was small (0.14 eV), leading to kinetically similar formation rates. Sun et al.^[92] uniformly encapsulated Rh within NaX zeolite crystals *via* an *in situ* synthesis. The formed Si–O–Rh bonds enhanced catalytic activity and Rh leaching resistance (only 1.0×10^{-7} Rh loss after 5 cycles), achieving a TOF of 6588 h^{-1} for 1-hexene hydroformylation. However, regioselectivity remained low (n/i ratio = 0.73), which improved to 2.59 when combined with PPh_3 to introduce steric hindrance.

These studies focused on achieving high dispersion and stabilization of Rh but did not fully exploit the microporous structure's impact on regioselectivity. Therefore, modifying and precisely tuning zeolite pore channels are necessary to enhance the confinement effect of zeolitic pores. Zhang et al.^[93] prepared a $\text{Kx}^{\wedge}\text{Rh@S-1}$ catalyst *via in situ* synthesis for propylene hydroformylation. K doping enhanced the steric confinement microenvironment around Rh clusters within zeolite pores, changing propylene adsorption from dual-site to single-site mode, promoting terminal CO insertion for higher linear aldehyde selectivity. The catalyst achieved high activity (TOF = 7328 h^{-1}) and regioselectivity (n/i ratio = 5) at 85°C and 5 MPa, with stable operation for 280 h in a fixed-bed reactor. However, precise control of the K/Rh ratio was required, as excess K blocked zeolite pores and covered Rh active sites, leading to decreased CO adsorption and reaction TOF (Figure 5(c)). Studies show that when Rh atoms are uniformly distributed on both internal and external surfaces of zeolites, the low activation energy (60–90 kJ/mol) of hydroformylation leads to fast reaction kinetics. Consequently, the diffusion resistance within the zeolite pores becomes relatively significant, limiting mass transfer of reactants to the internal active sites. In this case, the contribution of Rh sites on the external surface to the overall catalytic reaction is amplified. However, these external Rh sites lack the spatial confinement effect, resulting in weaker control over reaction intermediates and thus diminished regioselectivity (n/i ratio). In light of this, Zhang et al.^[94] prepared a Rh@MEL catalyst *via* hydrothermal synthesis, confining Rh species within MEL zeolite pores ($5.3 \text{ \AA} \times 5.4 \text{ \AA}$) for propylene hydroformylation. The pore confinement stabilized linear intermediates (Figure 5(d)), achieving an n/i ratio of 5. However, the small number of Rh species (~3%) on the external surface still limited further improvement of regioselectivity. Therefore, 2,4-dimethylbenzenethiol (DMBT, kinetic diameter $8.1 \text{ \AA}$) was introduced into the reaction system to selectively poison the external surface Rh sites (Figure 5(e)). When the DMBT/Rh ratio was 8.0, the n/i ratio reached as high as 110, with a TOF of 6500 h^{-1} , dramatically enhancing regioselectivity while maintaining high activity. Recently, Dou et al.^[95] achieved a breakthrough by selectively confining sub-nanometer Rh clusters within the sinusoidal 10-membered

ring channels of MFI zeolite. The MFI framework acts as a rigid ligand for the sub-nanometer Rh clusters, achieving high regioselectivity (n/i ratio = 400) in long-chain olefin ($\text{C}_6\text{--C}_{12}$) hydroformylation. For 1-decene hydroformylation, this catalyst achieved 98% conversion and an n/i ratio of 385, with regioselectivity further increasing to 582 at low conversion (7.3%). It also demonstrated superior regioselectivity for other α -olefins compared to most existing heterogeneous catalysts (typically <30).

Recently, zeolite-encapsulated rhodium carbides have been found to maintain high activity while achieving superior regioselectivity. Huang et al.^[96] prepared a zeolite-encapsulated rhodium carbide catalyst ($\text{RhC}_x\text{@S-1}$) *via* a one-pot hydrothermal synthesis combined with direct carburization reduction process. The *in situ* formed carbon species interacted with the zeolite silica framework to create Si–O–C structures, thereby precisely tuning the electronic and steric microenvironment of Rh active sites. The formed Rh-C_6 structure enhanced the positive charge of Rh, lowered the activation energy for linear aldehyde formation, and suppressed branched aldehyde formation. This catalyst exhibited high butanal formation rate ($3844 \text{ mol}/(\text{mol} \cdot (\text{Rh} \cdot \text{h}))$), chemoselectivity (83%), and regioselectivity (n/i ratio = 5.0) in propylene hydroformylation (85°C , 4 MPa), demonstrating good adaptability to substrates and recyclability with negligible Rh leaching. However, its high steric hindrance reduced regioselectivity for aromatic olefins like styrene (n/i ratio = 0.8).

1.5 Composite-supported catalysts

Beyond the aforementioned single-material catalyst supports, composite carriers with synergistic effects can leverage the advantages of different materials to enhance the performance of heterogeneous hydroformylation reactions. Chen et al.^[97] constructed a core-shell $\text{Rh}/\text{ZnO}_{50}\text{@ZIF-8}$ catalyst by *in situ* growth of ZIF-8 on a self-made ZnO_{50} for 1-dodecene hydroformylation. This design utilizes the ZIF-8 shell (pore size $\sim 3.4 \text{ \AA}$) as a molecular sieve-type physical barrier to effectively block the leaching of soluble carbonyl active species generated during reaction, thereby significantly improving catalyst stability. Experimental results showed that at 4 MPa, 90°C , for 2.5 h, the uncoated $\text{Rh}/\text{ZnO}_{50}$ catalyst achieved an initial conversion of 92.4% but dropped to 65.2% after the second cycle with 18.2% Rh leaching. In contrast, $\text{Rh}/\text{ZnO}_{50}\text{@ZIF-8}$ maintained nearly unchanged conversion (99.1%) and chemoselectivity (71.0%) over four consecutive cycles, with Rh leaching reduced to only 0.55%. Moreover, this composite catalyst demonstrated excellent universality for various long-chain olefins (e.g., 1-hexene, 1-octene), fully confirming the critical role of the ZIF-8 shell in suppressing metal leaching and preserving the integrity of active catalytic sites, although its preparation process is relatively complex. Wei et al.^[98] prepared a CoO@C|SBA-15 composite catalyst using an impregnation-carbonization

method, confining CoO nanoparticles (5 nm) coated with a carbon layer (2.5 nm) within the mesopores (7.2 nm) of SBA-15. After reduction, electron transfer between metal Co and the carbon layer promoted the adsorption and activation of CO and H₂ at the Co/C interface, thereby enhancing the CO insertion reaction. Additionally, the carbon layer provided a physical protective barrier for Co nanoparticles, inhibiting their leaching under reaction conditions (Figure 6(c)). Consequently, this catalyst achieved 100% conversion of 1-hexene and exhibited good cycling stability at 120 °C and 5 MPa.

2 Design principles and challenges of catalyst supports

Currently, significant progress has been made in the research on supports for heterogeneous hydroformylation catalysts, and a comparison of these different types of supports is shown in Table 1. These categories of supports significantly influence the catalytic performance through properties such as surface chemistry and pore confinement effects. In brief, each class of support for heterogeneous Rh hydroformylation catalysts presents a distinct set of advantages and challenges. Inorganic oxides (e.g., SiO₂, CeO₂) offer tunable porosity and leverage surface chemistry/SMSI to modulate Rh electronic states, enhancing activity and stability. Their principal challenge lies in balancing activity and selectivity when using ligands, which often suffer from leaching or diffusion limitations. Carbon materials (e.g., CNTs, graphene) provide high surface area and chemical stability, and their surface can be functionally tailored to influence Rh sites. A key strength is enabling sophisticated hybrid or bimetallic architectures for exceptional activity and stability. However, they struggle with intrinsic poor regioselectivity, and the advanced structures required for high performance involve complex, multi-step syntheses that hinder scalable production. Porous organic polymers represent a paradigm shift by integrating ligands directly into the scaffold, creating a homogeneous-like, precise coordination environment for Rh that achieves superb regioselectivity and inhibits leaching. The core

challenge is the intricate, multi-variable synthetic optimization needed (e.g., ligand ratios, P/Rh) to balance performance, complicating reproducibility and scale-up. Zeolites uniquely provide molecular-scale shape selectivity via uniform micropores, using powerful confinement effects to achieve very high regioselectivity and stabilize encapsulated Rh. Their effectiveness is highly dependent on precise structural control to manage inherent issues: external surface sites degrade selectivity, and micropores can impose diffusion limits on activity. Composite supports are engineered to combine material properties synergistically, enabling multifunctional designs (e.g., core-shell structures) that enhance stability and selectivity. The pursuit of these advanced architectures, however, introduces significant synthetic complexity, making the development of scalable and cost-effective fabrication methods a major hurdle.

Regarding catalytic activity, enhancing the dispersion and accessibility of Rh active sites, along with modulating their electronic properties, are crucial^[20,99]. From a design principles perspective, optimizing activity focuses on maximizing active site accessibility and electronic tuning. Supports must provide anchoring points for atomic-level Rh dispersion while serving as electronic modulators to optimize adsorption strengths and lower activation barriers. In recent years, utilizing supports with high specific surface areas and porous structures to improve the dispersion of Rh active phases has become a prominent research focus. The speciation of Rh metals and their oxides is evolving from nanoparticles to nanoclusters and ultimately atomically dispersed species^[26,37]. This advancement has increased the turnover frequency (TOF) values from below 1000 h⁻¹ in early studies to above 6000 h⁻¹ based on metal active sites, even rivaling the activity of homogeneous catalysis^[50,60]. In terms of support selection, inorganic oxides and carbon-based supports require abundant surface hydroxyl groups or oxygen vacancies to anchor Rh metal. Porous organic polymers need sufficient phosphine ligands to coordinate with Rh atoms. For zeolite supports, organic amine ligands must be introduced during *in situ* synthesis to prevent Rh precipitation under alkaline conditions^[37,100]. Modulating the electronic properties of Rh can also enhance its catalytic activity^[20,101–102].

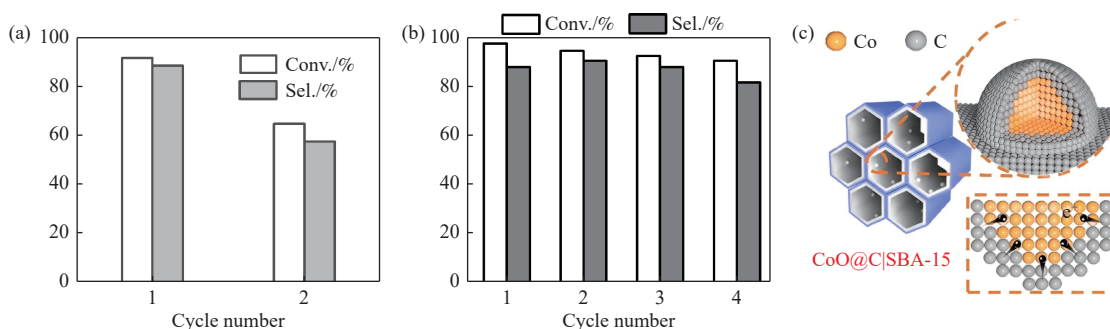


Fig. 6 (a) Stability test of Rh/ZnO₅₀ catalyst (reaction conditions: 0.10 g catalyst, 4 MPa, 90 °C, 2 h, 2.5 mmol 1-dodecene, 1.0 mmol 1-octanol (internal standard))^[97]; (b) Stability test of Rh/ZnO₅₀@ZIF-8 catalyst (reaction conditions: 0.10 g catalyst, 4 MPa, 90 °C, 4.5 h, 2.5 mmol 1-dodecene, 1.0 mmol 1-octanol (internal standard))^[97]; (c) Schematic illustration of CoO@C|SBA-15^[98] (with permission from RSC and Elsevier)

Table 1 Advantages and challenges of heterogeneous hydroformylation catalyst supports^[44–59,63–67,69–71,79–87,89–98]

Support Type	Support name	Advantages	Challenges
Inorganic oxides	Rh/SiO ₂	High specific surface area, macroporous structure, high yield	Reduced substrate accessibility due to phosphine ligands
	Rh/SBA-15	Tunable pore size, excellent stability	Phosphine ligand leaching
	Rh-UFSi	Promotes olefin adsorption, elevated Rh electron density, reduced ligand leaching	Limited regioselectivity control
	Rh-Co/SiO ₂	Synergistic bimetallic effect	High reaction energy consumption
	Rh/Cu ₂ O	Interfacial electron transfer; high Rh leaching resistance	Excessive CO adsorption, low regioselectivity
	Rh/nano-ZnO	High reactivity	Weak surface acidity, low regioselectivity
	Rh/CoO	Electron-rich Rh sites <i>via</i> SMSI, CoO _x -overlayer induced confinement	Not specified
Carbon-based materials	Rh1/CeO ₂ -Rod	High reactivity, high regioselectivity	Synthetic challenge in facet control
	Rh/AC	High activity, high regioselectivity	Low product regioselectivity
	Rh/RGO	High dispersion, high exposed surface area, good activity, excellent product regioselectivity	Not specified
	S1/Rh/AC	Enhanced product regioselectivity	Complex membrane coating process, precise pore size control
	PPh ₃ -Rh/RGO	High Rh dispersion, steric hindrance (PPh ₃), favored linear pathway	Low thermal stability
	PPh ₃ -RhAC-SA/N-C	Good thermal stability; high catalytic activity; excellent product regioselectivity	Complex synthesis process, limited scalability
	Co@N-CNTs/RhP	The unique structural design leads to ultra-high activity and stability in the reaction	Not specified
	Rh/CNFs	High reactivity	Severe metal leaching
	PG/PU-NIXANTPHOS-Rh(I)	Good cycle stability	Active-site shielding, reduced reactivity
	Rh/POL-PPh ₃	High specific surface area, high activity, good stability	Low product regioselectivity
Organic porous polymers	Xantphos-Rh/POPs-PPh ₃	Enhanced regioselectivity, good catalyst stability	Low activity, precise control of the Xantphos/PPh ₃ ratio
	Rh/CPOL-bp&P	High specific surface area, large pore volume, high activity, good product regioselectivity, good stability	Precise Biphephos/PPh ₃ ratio required
	Rh/POP-PhPh ₃ -BP-P(OPh) ₃	Enhanced catalytic activity and stability, good product regioselectivity	Precise ligand concentration control required
	Rh/POL-BPa&PPh ₃	Bimodal pore size distribution, high specific surface area, high activity, good product regioselectivity, good stability, low metal leaching	Not specified
	Rh/phosphite-POP	Exceptional structural integrity, negligible Rh leaching, stable reaction pathways, sustained optimal yield	Essential requirement: P/Rh ≥ 9
	Rh@S-1	Suppression branched aldehydes, enhanced regioselectivity	Incomplete Rh encapsulation, low stability
Zeolite	Rh@S-1	High hydrophobicity for olefin enrichment, superior conversion over impregnated catalysts	Not specified
	Rh@Y	High activity, superior stability	Large pore size (0.71 nm), weak confinement effect, low product regioselectivity
	Rh@NaX	Excellent activity and stability, minimal metal leaching	Dependent on PPh ₃ combination
	Kx ⁺ Rh@S-1	Enhanced steric microenvironment, promoted activity, regioselectivity and stability	Narrow operating window for K/Rh ratio
	RhC _x @S-1	Precise microenvironment control, excellent activity, regioselectivity and stability	Low regioselectivity for styrene

Table 1 Advantages and challenges of heterogeneous hydroformylation catalyst supports^[44–59,63–67,69–71,79–87,89–98] (Continued)

Support Type	Support name	Advantages	Challenges
Composite support	Rh-MEL	Exceptional regioselectivity, broad alkene applicability, superior to state-of-the-art heterogeneous catalysts, enhanced selectivity at low conversion	Not specified
	Rh@MEL	Synergistic effect of pore confinement and surface selectivity, significantly enhanced regioselectivity and specificity	Detrimental effect of surface Rh (approximately 3%) on regioselectivity
	Rh/ZnO ₅₀ @ZIF-8	Molecular-sieve barrier against leaching, high activity, selectivity and stability, broad applicability to long-chain alkenes	Complex preparation process
	CoO@C SBA-15	Carbon-layer physical barrier against Co leaching, high activity and stability	Complex preparation process

The Rh active sites in heterogeneous catalytic systems follow reaction steps similar to homogeneous hydroformylation, including adsorption of reactants (olefin, CO, H₂) on Rh sites, H₂ dissociation into active H atoms, H insertion, and CO insertion. The adsorption strengths of different species on Rh sites affect the rates of these steps, thereby influencing the overall catalytic activity. Thus, precise control over the electronic structure of Rh sites through heteroatom doping (e.g., P, N, Co) is essential for boosting reactivity^[50,54,60].

In terms of product selectivity, controlling reaction conditions and enhancing spatial confinement effects at active sites are critical^[20,63,82]. Selectivity control is achieved through geometric constraint. The support architecture acts as a “solid ligand,” creating tailored microenvironments that discriminate between linear and branched pathways *via* molecular sieve effects, steric guidance, or physical barriers. Balance is essential to avoid impeding mass transport. Studies indicate that although elevated temperatures and prolonged reaction times improve conversion rates, high temperatures promote alkene isomerization (converting α -olefins to internal alkenes) and aldol condensation of aldehyde products, thereby reducing chemoselectivity, particularly when the support contains acidic sites^[20,88,103–104]. The spatial confinement effect imparted by the support around Rh sites is a key factor for regulating activity and regioselectivity, as it restricts intermediate geometry and orientation to influence reaction pathways and transition state energy^[47,59]. When alkenes adsorb on Rh *via* the terminal carbon, linear alkyl intermediates are favored, leading preferentially to linear aldehydes. Therefore, enhancing the confinement environment around Rh centers can selectively stabilize linear alkyl intermediates (which are slenderer) while hindering the formation or stabilization of bulky branched alkyl species, thereby improving regioselectivity^[20,60,67,94–95,105]. Confined cavity structures can also stabilize Rh nanoparticles and isolated Rh atoms, enhancing the dispersion and stability of Rh sites^[20,101,106]. Additionally, for catalysts with Rh distributed in both bulk and external surfaces, selectively poisoning Rh sites on external surfaces outside spatial confinement environments is a key strategy for improving regioselectivity^[94]. However,

it is noteworthy that excessive confinement by narrowing pore sizes can lead to slow reactant diffusion or reduced accessibility to active sites, potentially lowering the overall reaction activity^[48–49,107].

Metal leaching of active components is the primary cause of deactivation in Rh-based heterogeneous catalysts, while sintering, coking, and ligand/support degradation also contribute to activity loss^[47,70–71,81,89,97]. Stability assurance relies on robust architectural design. Durable chemical anchors—through covalent bonds or multidentate coordination—and physical confinement prevent Rh loss and degradation under harsh conditions. Key strategies for improving stability include immobilizing Rh atoms through strong metal-support interactions to prevent migration and aggregation, or introducing stabilizing ligands or functional groups^[46,71,82,84]. For example, surface defects (e.g., oxygen vacancies, nitrogen vacancies) on supports can form covalent bonds (e.g., Rh-O-Si, Rh-N-C) with Rh to strengthen metal-support interactions. Alternatively, grafting phosphine ligands, N-heterocyclic carbenes (NHCs), or N/O-containing functional groups onto support surfaces creates multidentate coordination structures with Rh, effectively reducing Rh leaching during reactions^[70,90–91].

In summary, the reaction performance of Rh-based heterogeneous hydroformylation catalysts for olefins can be effectively improved through the design of supports and active sites, pore structure and microenvironment modulation, chemical modification, and process optimization. The core challenge integrates these three principles: activity optimization, selectivity control, and stability assurance. Advanced designs employ multifunctional architectures to balance competing demands through precise nanoscale microenvironment engineering. However, developing catalysts that simultaneously exhibit high activity, chemo-/regioselectivity, and stability remains a significant challenge.

3 Conclusion and outlook

The support material for heterogeneous hydroformylation rhodium catalysts exerts a profound influence on the catalytic activity, chemoselectivity/regioselectivity, and

catalyst stability in olefin hydroformylation. Current research on supports for Rh-based heterogeneous hydroformylation catalysts has evolved from traditional supported materials toward functionalized, confined, and atomically precise designs. It is observed that inorganic oxide supports offer high specific surface area and structural tunability, yet face challenges including ligand and active metal leaching, as well as inadequate control over regioselectivity. Carbon-based materials serve as excellent substrates for achieving high dispersion of active metals, though surface modification is often required to optimize product regioselectivity. Hierarchically porous organic polymers, featuring multi-level pore structures and synergistic ligand effects, significantly enhance regioselectivity; however, their synthesis is complex and requires precise control over ligand-to-Rh ratios. The intrinsic micropore confinement effect of zeolites improves regioselectivity, yet challenges such as external metal leaching and pore diffusion limitations must be addressed. Composite supports, by providing physical barriers and synergistic effects, can enhance catalytic stability and general applicability, although their preparation processes are intricate. In the future, support design will transition from a “passive support” role to “active regulation,” focusing on single-atom/cluster catalysis, hierarchical pore structure modulation, and tailored active-site-support matching to synergistically optimize activity, selectivity, and stability. In summary, industrially oriented applications will drive catalyst development toward low cost, renewability, and extended lifespan, with multifunctional supports combining confinement effects and strong metal-support interactions emerging as key to achieving breakthroughs in the industrial implementation of heterogeneous hydroformylation.

Declaration of Competing Interest

The authors declare no conflict of interest.

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烯烃多相氢甲酰化铑基催化剂载体研究进展

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摘 要: 烯烃氢甲酰化反应作为合成高附加值醛类的关键工艺, 其应用范围已从短链烯烃扩展至长链烯烃(C₆₊)。传统均相催化体系面临贵金属 Rh 难分离回收等挑战, 烯烃氢甲酰化多相催化体系成为研究热点, 通过催化剂载体设计可有效解决上述问题。本工作综述了多相 Rh 基催化剂载体的研究进展, 重点分析了无机氧化物负载催化剂、多孔炭负载催化剂、有机多孔聚合物基催化剂、分子筛负载催化剂及复合载体负载催化剂的结构调控策略对活性位点分散性、区域选择性及循环稳定性的影响, 旨在为多相催化剂的理性设计提供相关参考。

关键词: 氢甲酰化; 多相催化; 载体设计; 长链烯烃; 醛

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