

Recent advances in catalysts for the highly selective conversion of syngas into para-xylene

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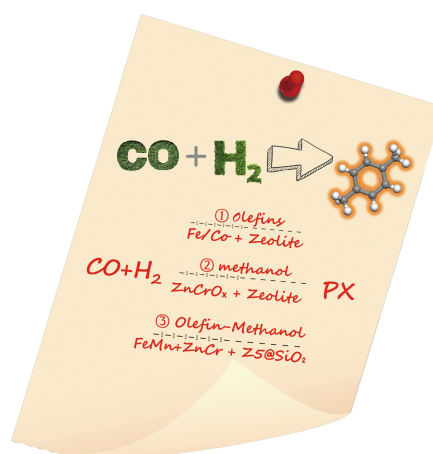
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Abstract: Para-xylene (PX), as a pivotal chemical feedstock, plays an indispensable role in ensuring nation energy strategic security and propelling the low-carbon and green development of the chemical industry. The review systematically summarizes the recent advancements in catalysts for the direct conversion of syngas into *p*-xylene-enriched aromatics, focusing on three distinct catalytic systems: the Fischer-Tropsch synthesis catalyst/zeolite coupling system, the methanol synthesis catalyst/zeolite synergistic system, and the dual engine driven/zeolite catalytic system. Through a comprehensive and in-depth analysis of critical parameters, including the electronic structure features of active components, the synergistic action mechanism of promoters, and the pore topology of zeolite within each catalytic system, the governing principles of catalytic activity, selectivity, and stability are thoroughly revealed. Simultaneously, based on the reaction intermediate evolution pathways, the reaction mechanisms involving olefin, methanol, and olefin-methanol dual intermediate routes are systematically explored. The current scientific bottlenecks confronted by the catalyst systems, such as the intricate challenge of achieving coordinated optimization of activity and stability, and the lack of clarity in the regulatory mechanism of PX directional selectivity, are meticulously expounded. Building upon these identified issues, prospective research directions are comprehensively summarized.

Key words: para-xylene; syngas; the Fischer-Tropsch synthesis; methanol; the reaction mechanisms



As a key aromatic compound, PX is extensively utilized in the manufacture of high-performance plastics, advanced synthetic fibers, and specialty chemicals^[1–7]. Driven by the rapid development of the polyester industry, PX consumption in China has demonstrated consistent growth. In 2024, consumption reached 40 million tons, accounting for 63% of the global total, while the import dependency rate remained as high as 17%, underscoring a substantial gap in domestic supply. At present, global production of PX remains heavily dependent on naphtha-based catalytic cracking technology. However, China's energy structure characterized by abundant coal reserves but scarce oil and

limited natural gas, conventional petroleum-derived routes face dual challenges: ensuring security of feedstock supply and mitigating cost volatility^[8–14]. In contrast, syngas represents a versatile chemical feedstock with diverse sources. The development of technologies for converting syngas to PX-rich aromatic mixtures can effectively extend the industrial chain, enhance economic returns, lessen dependence on imported petroleum resources, strengthen national energy security, and contribute to building a low-carbon, environmentally benign, and sustainable chemical industry. These advantages align with China's strategic goals for energy security and green development.

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Currently, two primary pathways are explored for syngas highly selective conversion to PX. The first is the modified Fischer-Tropsch (FT) pathway: syngas is initially converted into olefins intermediates, which subsequently undergo oligomerization, cyclization, and dehydrogenation to PX^[15–22]. The second is the methanol-mediated pathway: syngas is first transformed into methanol, which is then converted to PX^[23–29]. In both routes, the catalyst serves as the core of the process, with its performance directly determining the reaction efficiency and product distribution. Critical factors governing catalytic performance include the choice of active metal and promoter, modulation of zeolite acidity and pore architecture, and the coupling mode between metal and zeolite components^[30–35]. While numerous studies have reported catalysts for syngas and even CO₂ conversion to aromatics^[36–40], recent reviews have primarily provided macroscopic summaries of mixed aromatic products or focused on the FT pathway^[4,17–18,23,41–42], leaving a gap concerning highly selective PX production.

This review systematically compiles and compares the structure-activity relationships and selectivity control mechanisms of three major catalytic systems the “olefin intermediate pathway”, the “methanol intermediate pathway”, and the emerging “olefin-methanol dual-engine pathway” for the directional synthesis of PX from syngas. It aims to achieve a targeted shift from mixed aromatics to high-value PX, offering more focused and forward-looking insights into catalyst design, mechanistic understanding, and process engineering. Thereby, it addresses the current lack of comprehensive reviews on high-selectivity catalysts for syngas to PX conversion. Given the significance of catalytic materials in this field, this article systematically summarizes different catalytic systems, discusses underlying reaction mechanisms, and provides perspectives on remaining challenges and future directions.

1 Fischer-Tropsch synthesis catalyst-zeolite coupled catalytic systems

1.1 Fe-based catalyst-zeolite coupled catalytic systems

Fe-based catalysts are predominant in Fischer-Tropsch Synthesis (FTS) due to their high activity in activating CO and H₂, cost-effectiveness, and earth abundance^[43–51]. When coupled with zeolites, which provide unique shape-selective catalysis and acidic functions, bi-functional systems can be engineered for the targeted production of PX from syngas. The zeolite component not only facilitates the conversion of primary FTS intermediates but also suppresses undesired side reactions. This synergy between Fe-based catalysts and zeolites has emerged as a promising strategy for the high-selectivity synthesis of aromatics, particularly PX, making it a focus point in syngas conversion research. Understanding the synergistic mechanisms and recent advancements in these coupled systems is crucial for advancing the value-added utilization of syngas.

The interaction between the metallic Fe sites (especially iron carbides) and the Brønsted acid sites of the zeolite is central to the performance of these bi-functional systems. The proximity and intimacy of contact between the two components critically affect the diffusion and subsequent conversion of reactive intermediates, such as olefins, and ultimately influence product distribution. Catalyst design strategies aim to optimize metal-zeolite interaction. For instance, Xu et al.^[52] investigated Fe/HZSM-5 composite catalysts and found that increasing Fe loading modulated the catalyst's acidity, enhancing the synergy between active Fe species and the zeolite. However, excessive loading led to carbon deposition, degrading activity and stability. Subsequently, they designed an eggshell-structured catalyst with FeMn nanoparticles as a “yolk” inside a hollow HZSM-5 “yolk” shell^[53], as shown in Figure 1(a). This design harnessed control to facilitate the diffusion of olefins intermediates toward acidic sites, thereby fully leveraging the shape-selective and aromatization capabilities of HZSM-5. The hollow structure and mesoporous channels shortened the diffusion path, significantly suppressing carbon deposition and achieving a high aromatic yield 1.9 g/(g·h) with remarkable stability over 100 h.

The addition of promoters to Fe-based catalysts coupled with zeolites can significantly enhance CO conversion and aromatic selectivity. Fu et al.^[54] reported a composite system of Fe/ZnCr₂O₄ and HZSM-5. Introducing 3% Fe onto ZnCr₂O₄ significantly boosted CO conversion without sacrificing aromatic selectivity, achieving 57.5% CO conversion and 74% aromatic selectivity. The promoters facilitated the formation of oxygen vacancies and highly dispersed iron carbide species, which promoted CO activation and the generation of oxygenated intermediates. These intermediates were then efficiently converted to aromatics within HZSM-5, addressing the challenge of simultaneously achieving high conversion and selectivity. Similarly, Saif et al.^[55] developed an FeZnMg/HZSM-5 system *via* co-precipitation. Their study detailed the synergistic roles of Zn and Mg promoters: Zn formed a spinel structure (ZnFe₂O₄), enhancing the reduction of iron oxide, while Mg improved the dispersion of active sites, modified the Fe lattice, and strengthened CO adsorption, thereby suppressing CO₂ and light alkane formation. Through parameter optimization, this system achieved 97% CO conversion and 52% aromatic selectivity by enhancing the formation of active iron carbide. In another study, Kang et al.^[56] prepared a series of K/FeMn catalysts and systematically studied the effect of Mn promoters. They found that Mn addition improved the dispersion of Fe₃C₃ particles. An optimal Mn/(Fe+Mn) ratio of 60% achieved 97.2% CO conversion and 39.8% aromatic selectivity at 340 °C and 2 MPa.

Innovative catalyst architectures are being explored to address common issues like metal sintering and weak metal-zeolite interactions. Wang et al.^[57] developed a pitaya-like Fe-MFI composite catalyst using an organosilane modification strategy.

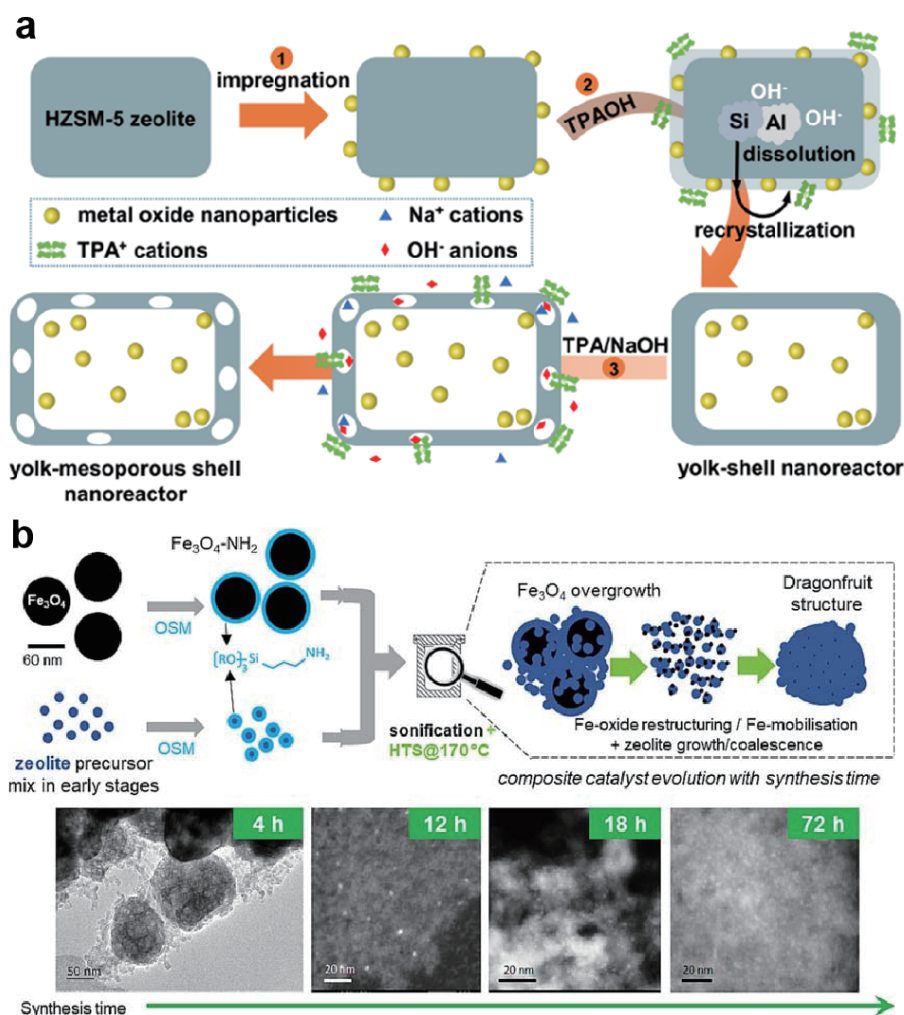


Fig. 1 (a) Formation mechanism of the yolk@mesoporous shell nanoreactor^[53]; (b) Hydrothermal synthesis method and catalyst structure^[57] (with permission from Elsevier)

This design uniformly dispersed 1–4 nm Fe₃O₄ nanoparticles within a mesoporous ZSM-5 zeolite, creating a structure where the small Fe₃O₄ nanoparticles (“fruit granules”) were embedded in the zeolite “pulp” (Figure 1(b)). This configuration ensured strong interaction between the nanoparticles and the zeolite, yielding 42.6% CO conversion, 62% aromatics (among hydrocarbons) selectivity, and a high aromatic yield of 214 mmol_{aromatics}/(g·h). Notably, the catalyst exhibited exceptional anti-sintering properties and stability for 570 h, providing a novel approach to designing robust oxide-zeolite composite catalysts.

1.2 Co-based catalyst-zeolite coupled catalytic systems

Co-based catalysts are particularly advantageous for FTS targeting liquid fuels, owing to their exceptional hydrogenation activity, high selectivity toward long-chain hydrocarbons, and remarkable stability. They efficiently produce C₅₊ long-chain alkane with minimal by-product

formation^[58–59]. When coupled with zeolites, which offer tunable pore architectures and acidic properties, the resulting bi-functional system enables precise secondary conversion of the primary FTS products. This synergy between the two components allows for the coordinated regulation of “carbon chain growth” on the metal sites and subsequent “product tailoring” on the acid sites. Such a configuration effectively circumvents the product distribution limitations imposed by the Anderson-Schulz-Flory (ASF) model, thereby enhancing the selectivity, yield of desired products and opening a promising avenue for the high-value utilization of syngas. Elucidating the interaction mechanisms within these coupled systems is crucial for advancing FTS technology.

A notable demonstration of this strategy was reported by Wang et al.^[58], who developed a bi-functional catalyst comprising CoMnAl oxides and a core-shell HZSM-5@silicalite-1 zeolite. This system achieved impressive performance under mild conditions (280 °C, 2 MPa): CO conversion exceeded 70%, aromatic selectivity reached over 63% (with PX comprising 34.7% of the aromatic fraction),

while methane selectivity was maintained below 2.9%. Furthermore, the catalyst exhibited exceptional stability for more than 700 h. The high performance was attributed to the hierarchical hollow structure of the zeolite, which facilitated the diffusion of intermediates and products. The silicalite-1 shell played a critical role by passivating external acidic sites, thus suppressing undesirable side reactions, modulating acid site density, and optimizing the ultimate aromatic distribution. This study also highlighted the role of oxygen-containing aromatic compounds as key intermediates. By achieving efficient conversion under relatively mild conditions, this work addresses significant challenges in direct convert syngas into aromatics, including catalyst deactivation, low target product selectivity, and demanding reaction temperatures, offering valuable insights for designing high-performance bi-functional catalysts.

2 Methanol synthesis catalyst-zeolite synergistic systems

In contrast to FTS catalysts, metal oxides used in the methanol-mediated pathway due to abundant surface oxygen species and lattice defects. These features enable efficient activation of CO and H₂ molecules in syngas, precise regulation of C–O bond cleavage and recombination, minimal by-product formation, and enhanced selectivity toward target products^[60–64]. When coupled with zeolites, which function as nanoscale “molecular reactors”. The well-

defined mesopores of zeolites provide shape-selective confinement for reaction intermediates, suppressing the formation of large-molecular-weight by-products. Simultaneously, the acidity and pore architecture of the zeolite effect carbon-chain growth and aromatization pathways. This “precision supply of intermediates and size confinement of products” effectively overcomes the product distribution limitations inherent to traditional FTS, leading to a significant increase in PX selectivity.

A pivotal advancement was reported by Zhang et al.^[65], as shown in Figure 2(a) and Table 1, who developed a Cr/Zn-Zn/Z5@S1 catalyst for the one-step conversion of syngas to PX. The core innovation was a core-shell Zn/Z5@S1 zeolite, where a non-acidic silica-alumina shell passivates external acid sites, thereby inhibiting xylene isomerization side reactions. This system achieved 55.0% CO conversion with a PX selectivity of 27.6% among all products, and an impressive 77.3% selectivity for PX among xylene isomers. This work demonstrated that precise architectural design of the zeolite component is crucial for steering the reaction toward the desired product.

Further exploring the impact of zeolite morphology, Yang et al.^[66] constructed a bifunctional system of ZnCrO_x and sheet-like ZSM-5. They discovered that aromatic selectivity increased significantly as the crystal’s aspect ratio decreased. Characterization revealed that the shortened diffusion path along the *b*-axis of the plate-like crystals enhanced the diffusion of aromatic molecules, effectively suppressing secondary reactions within the pores.

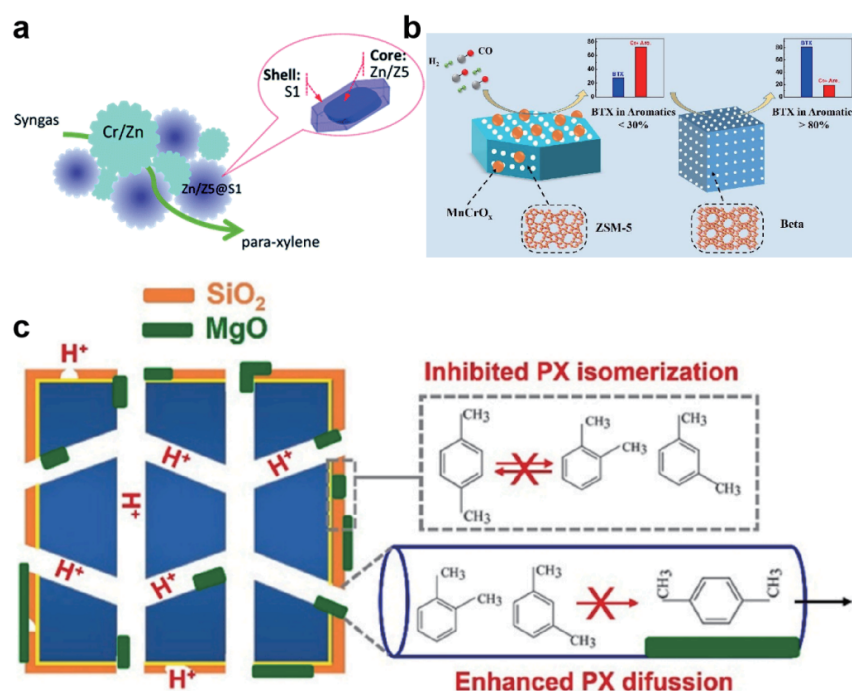


Fig. 2 (a) Illustration of the one-pass selective conversion of syngas to PX over the designed hybrid catalyst Cr/Zn–Zn/Z5@S1^[65]; (b) Schematic diagram of the catalytic reaction mechanism over the ZnCrO_x/ZSM-5 composite catalyst^[67]; (c) Schematic representation of the enhanced PX selectivity achieved by effective surface silylation followed by MgO loading^[71] (with permission from Elsevier)

Table 1 Performance data of typical composite multifunctional catalytic systems in the synthesis of PX-enriched aromatics from syngas

Catalyst	CO conv./%	Selectivity/%			Reference
		aromatics	PX	PX/X	
Cr/Zn-Zn/Z5@S1 hybrid	55.0	–	27.6	77.3	[65]
ZnCrO _x -ZSM-5-2.8	18.3	69.0	4.6	25.3	[66]
MnCr-ZSM-5+Beta	30.7	43.7	27.1 (BTX)	85.7 (BTX/Aro.)	[67]
Cr ₂ O ₃ +Ga-ZSM-5@SiO ₂	27.6	70.3	25.3	71.1	[68]
MnCrO _x -SAPO-34-ZSM-5	21.9	64.7	–	76.8	[69]
1.0%FeMn&[ZnCr&Z5@SiO ₂]	59.0	19.0	6.2	72.7	[72]

This study provided direct experimental evidence that crystal morphology engineering is a viable strategy for enhancing catalytic performance in syngas to aromatics. Subsequently, the same group proposed a dual-bed system combining an MnCrO_x/ZSM-5 composite with Beta zeolite^[67]. The first bed converted syngas to aromatics, while the second bed containing Beta zeolite promoted the dealkylation of heavier aromatic intermediates (C₉₊), increasing the proportion of BTX (benzene, toluene, xylene) in the aromatic products to over 80% (Figure 2(b)). This approach addressed the key challenge of low BTX selectivity (<35%) in conventional OX-ZEO (oxide-zeolite) catalysts.

The strategic incorporation of promoters and additional zeolites can further optimize reaction pathways. Wang et al.^[68] designed a system comprising Cr₂O₃ and metal-doped zeolites. Among the dopants (Zn, Ga, La, Mg), Ga was found to significantly enhance performance, increasing CO conversion from 20.8% to 28.4% and the aromatic space-time yield to 34.6 g/(kg·h), with PX selectivity reaching 33.0%. Characterization and theoretical calculations indicated that Ga doping improved CO adsorption under high-pressure conditions and enhanced the conversion efficiency of methanol intermediates. In a different approach, Zhang et al.^[69] introduced SAPO-34 into the MnCrO_x-ZSM-5 system. SAPO-34 consumed ketene intermediates from the oxide, converting them to light olefins and thus inhibiting the methylation of BTX to heavier aromatics on the ZSM-5 acid sites. This maneuver increased the BTX selectivity within the aromatic fraction from 28.9% to 64.7%, resolving the conflict between high BTX yield and undesirable secondary reactions.

The principles of methanol-mediated synthesis have also been successfully applied for CO₂ conversion into PX. Tian et al.^[70] designed a ZnZrO_x/hollow tubular HZSM-5 tandem catalyst for CO₂ hydrogenation to PX. The hollow tubular morphology of HZSM-5, achieved *via* steam-assisted crystallization and combined with external surface passivation, contributed to excellent diffusion properties. The catalyst achieved 16.3% CO₂ conversion, 71.3% aromatic selectivity, and a PX proportion of 76.2% among aromatics, maintaining stability for 100 h. The reaction was confirmed to proceed *via* a methanol-mediated pathway. Pushing the boundaries of catalyst stability and selectivity, as shown in Figure 2(c), Murciano et al. employed large-crystal HZSM-5 and implemented a synergistic

modification strategy involving surface silanization and MgO loading^[71]. The large crystals provided inherent shape selectivity, while the introduction of mesoporous *via* desilication improved stability by preventing pore blockage. Sequential modification with tetraethyl orthosilicate (TEOS) to passivate external acid sites and loading of MgO to fine-tune acidity and pore environment ultimately yielded a high PX selectivity of 76.8% among xylenes. This multi-dimensional engineering approach presents a promising solution to the longstanding challenge of balancing high aromatic selectivity with long-term catalyst stability.

3 Dual-engine-driven and zeolite catalytic systems

To overcome the challenge of low space-time yield (STY) in the direct conversion of syngas into light aromatics particularly PX. Wu et al.^[72] developed an innovative “dual-engine-driven” (DED) catalytic system. This architecture integrates ZnCr-based “methanol engine”, FeMn-based “olefin engine” and a capsule-type Z5@SiO₂ zeolite (Figure 3). Within this configuration, the ZnCr component facilitates methanol synthesis from syngas, while the FeMn component promotes the formation of light olefins. These primary intermediates are then converted *in situ* within the Z5@SiO₂ zeolite, which functions as a shape-selective nanoreactor, guiding the transformation toward PX-rich aromatic mixtures. This cooperative mechanism effectively surpasses the limitations inherent to conventional single-pathway systems (e.g., sole methanol or olefin-mediated routes), which suffer from a trade-off between conversion and selectivity. Under optimized reaction conditions, the DED catalyst with a specific formulation of 1.0%FeMn&[ZnCr&Z5@SiO₂] demonstrated a remarkable PX STY of 36.1 g/(kg·h). This value is approximately eight times higher than that achieved by a traditional [ZnCr&ZSM-5] reference catalyst. The superior performance stems from the synergistic interplay between the two catalytic “engines”, which enhances the overall driving force for syngas conversion. Furthermore, the ZSM-5@SiO₂ zeolite, featuring a passivated external surface, plays a critical role by providing shape-selective confinement that favors the formation of PX while minimizing secondary reactions.

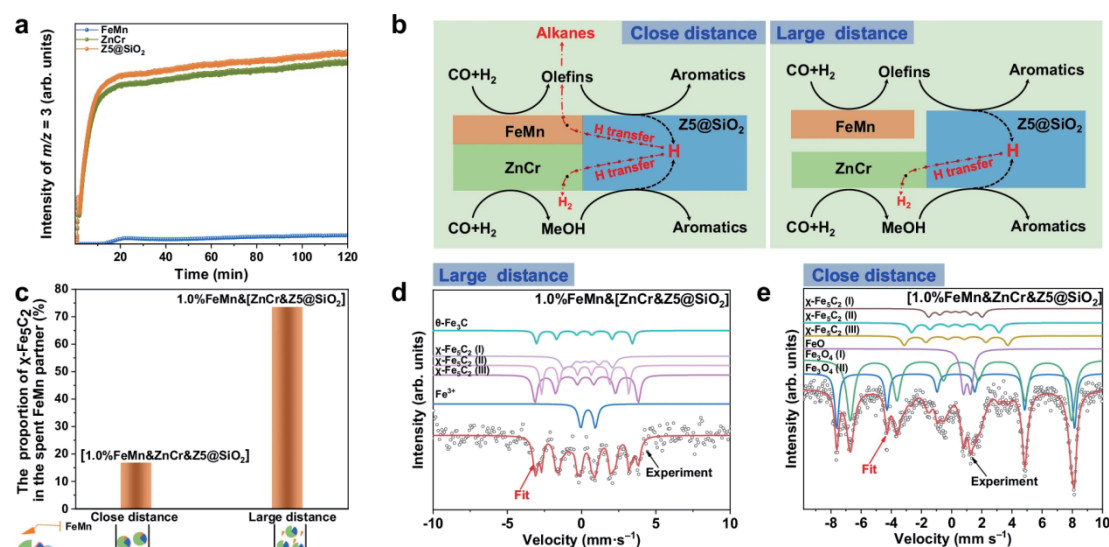


Fig. 3 The role of distance between FeMn, ZnCr and Z5@SiO₂^[72]
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A key design aspect involves the precise spatial organization of the functional components. Optimal performance is achieved by maintaining ZnCr in nanoscale proximity to the ZSM-5@SiO₂ zeolite to facilitate efficient hydrogen transfer, while the FeMn engine is positioned at a microscale distance. This deliberate arrangement helps prevent the over-hydrogenation of the valuable olefin intermediates. This sophisticated engineering of the reaction environment not only suppresses the formation of CO₂ as an undesired by-product but also significantly boosts the overall efficiency of the process, presenting a promising strategy for the high-yield production of PX from syngas.

4 Research on catalytic reaction mechanisms

The direct conversion of syngas into PX represents a strategically important route for producing high-value aromatics from non-petroleum resources such as coal, natural gas, and biomass. Despite making considerable progress in catalyst development, the intricate reaction mechanisms governing this process remain incompletely elucidated. A fundamental understanding of these mechanisms, including intermediate formation, diffusion, and conversion, is essential for the rational design of highly active and selective catalysts. Such insights not only help optimize reaction pathways toward PX but also provide a theoretical foundation for overcoming existing technical bottlenecks and accelerating industrial implementation.

4.1 Reaction pathway *via* olefin intermediates

In the complex reaction network for syngas-to-PX conversion, light olefins serve as pivotal intermediates that bridge C₁ species and aromatic products. Their formation

efficiency and subsequent conversion pathways critically influence both the overall process economics and the selectivity toward target aromatics. This section reviews recent advances in understanding reaction mechanisms centered on olefin intermediates. Yang et al.^[73] constructed a NaFeZrO₂/ZSM-5 tandem catalytic system for syngas conversion to aromatics. By correlating product distribution with CO conversion levels, the authors delineated a plausible reaction pathway over this bifunctional catalyst. Initially, CO hydrogenation proceeds on iron carbide (Fe₅C₂) active sites to generate light olefins and paraffins. These olefins then diffuse to the Brønsted acid sites of ZSM-5, where they undergo either oligomerization to form C₆₊ olefins or alkylation with light alkanes. The resulting longer-chain olefins are subsequently converted into aromatics *via* dehydrogenative aromatization, facilitated by Lewis acid sites within the zeolite. In a related study, Wang et al.^[58] investigated the aromatic formation pathway over a CoMnAl/HZSM-5@silicalite-1 (CMA/Hol-Z5-N) catalyst. They proposed that ethylene and C₃₊ olefins are first generated on Co₂C nanoprisms. A fraction of these olefins further react with CO on the zeolite acid sites to form oxygenated intermediates such as 2,4-dimethylbenzaldehyde. Simultaneously, higher oxygenates produced on the CMA component are converted to *p*-methylbenzaldehyde *via* aldol cyclization within HZSM-5. These carbonyl intermediates are hydrogenated and dehydrated to ultimately form aromatic products. At lower temperatures, HZSM-5 can directly convert *p*-methylbenzaldehyde to PX. Ethylene migrating into the zeolite pores also undergoes oligomerization, cyclization, and aromatization to yield cycloalkanes and aromatics (Figure 4). This work highlights the role of oxygenated aromatics as key cycle intermediates, offering a coherent mechanism that integrates both hydrocarbon and oxygenate pathways.

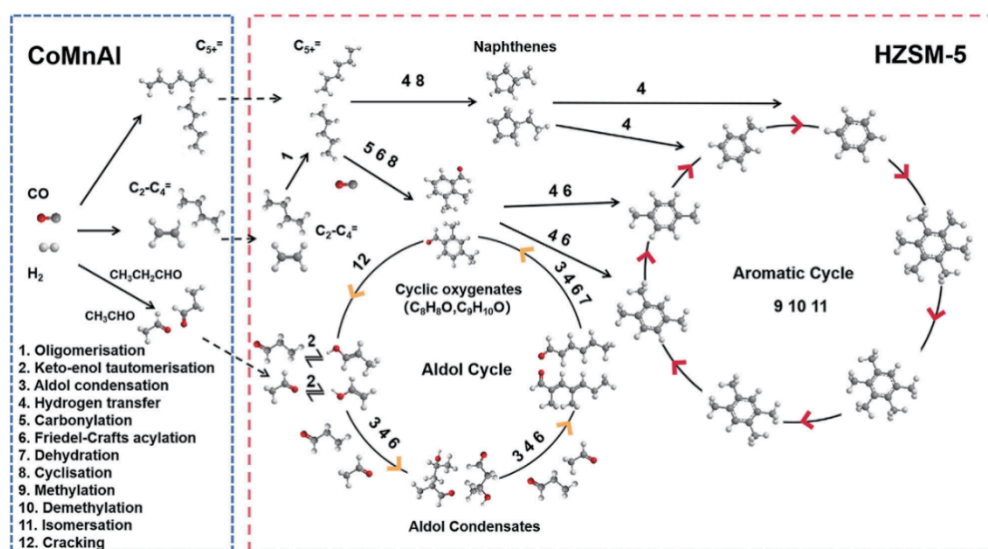


Fig. 4 Proposed reaction mechanism for the improved production of aromatics from syngas over the CoMnAl/HZSM-5 bifunctional catalysts^[58] (with permission from Elsevier)

4.2 Reaction pathway *v/a* methanol intermediates

In the direct conversion of syngas to PX, methanol intermediates act as key bridges linking syngas and the final aromatic products. The efficiency of their formation and subsequent conversion pathways critically governs both the overall CO conversion and the selectivity toward PX. A mechanistic understanding of the key elementary steps involving methanol intermediates is therefore essential for the rational design of catalysts-including the optimization of active site structure, electronic properties, and preparation methods and for guiding process optimization. This section involved the methanol-mediated reaction mechanism in syngas conversion, with an emphasis on analyzing the core factors that influence selectivity and efficiency, thereby providing a foundation for developing high-performance catalytic systems. Wang et al.^[68] proposed a composite system consisting of Cr₂O₃ coupled with Ga-doped H-ZSM-5 (Ga-ZSM-5@SiO₂). As an oxygen-vacancy-rich metal oxide, Cr₂O₃ facilitates CO activation on its surface vacancies. The process begins with the adsorption and activation of CO molecules, which then combine with activated hydrogen species to yield intermediates such as formaldehyde (HCO, H₂CO) and formate (HCOO). These species undergo sequential hydrogenation to form methanol, while a portion of the formaldehyde or formate intermediates may also diffuse into the zeolite pores to participate in subsequent transformations. The introduction of Ga significantly modifies the catalytic properties of H-ZSM-5. Framework Ga species enhance the CO adsorption capacity, increasing local CO coverage. More importantly, density functional theory (DFT) calculations revealed that Ga species, in synergy with a high-pressure CO atmosphere, substantially lower the energy barrier of the initial C-C coupling step in methanol conversion from 136 to 49 kJ/mol (Figure 5). This enhancement promotes the formation of C-C intermediates (e.g., acetyl groups) *via* methoxy

carbonylation, which subsequently undergo decarboxylation, aldol condensation, and cleavage reactions to form aromatics. Concurrently, the interplay between Ga Lewis acid sites and the Brønsted acid sites of the zeolite alters the hydrogen transfer pathway: the reaction shifts from a mechanism dominated by hydrogen transfer (which consumes olefin/cycloolefin intermediates) to one favoring dehydrogenation. Here, Ga sites abstract H⁻ from intermediates, which then combine with protons from Brønsted acid sites to form H₂, thereby minimizing intermediate loss and enabling the highly efficient and selective conversion of syngas into target aromatics.

The ternary composite catalytic system MnCrO_x-SAPO-34-ZSM-5, developed by Zhang et al.^[69], for the direct and selective conversion of syngas to high-value benzene, toluene, and xylenes (BTX). The primary innovation of this system lies in the establishment of a dual-pathway conversion mechanism for ketenes intermediates. One pathway involves the diffusion of ketenes into the pores of SAPO-34, where they are selectively converted to light olefins. Simultaneously, the remaining ketenes, along with the newly formed light olefins, migrate to the ZSM-5 component to undergo aromatization reactions, ultimately yielding BTX and other aromatic compounds. A critical function of this design is the effective suppression of secondary methylation of the primary BTX products. By selectively consuming a significant portion of the ketenes intermediates, SAPO-34 drastically reduces their concentration in the reaction milieu. This, in turn, minimizes the undesirable alkylation of BTX molecules with ketenes, a key side reaction that leads to the formation of heavier C₉₊ aromatics in conventional MnCrO_x-ZSM-5 binary systems. Furthermore, the structural intimacy between the SAPO-34, MnCrO_x and ZSM-5 components is crucial for ensuring efficient interparticle transfer of reactive intermediates and precise control over the reaction pathway.

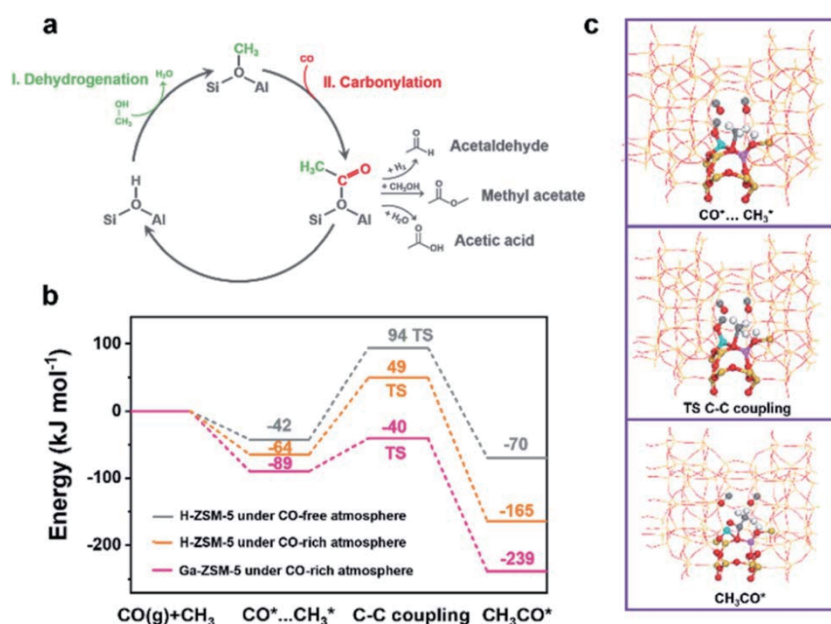


Fig. 5 (a) Koch carbonylation mechanism for the first C-C bond formation in the MTA reaction; (b) Free energy diagrams of the first C-C bond formation on H-ZSM-5 under a CO-free or CO-rich atmosphere and Ga-ZSM-5 under a CO-rich atmosphere; (c) The reaction scheme of the first C-C bond formation on Ga-ZSM-5 under a CO atmosphere^[68] (with permission from RSC Publications)

This engineered proximity enhances the synergistic interaction among the different functionalities. As a result, this ternary system significantly increases the BTX fraction within the total aromatic products from 28.9% to 64.7%, without compromising the overall aromatic selectivity, thereby achieving a marked shift in product distribution toward the more valuable BTX fraction.

4.3 Reaction pathway via olefin-methanol dual Intermediates

In addition to the well-established routes involving individual olefin or methanol intermediates, a synergistic catalytic pathway leveraging olefin-methanol dual intermediates has garnered significant research interest. This mechanism proposes that olefin and methanol intermediates do not operate independently; rather, they interact cooperatively to participate in C-C bond growth and aromatization processes. Such a dual-intermediate pathway offers a promising strategy for overcoming the thermodynamic limitations inherent in single-intermediate routes and enhances the selectivity toward valuable aromatics like PX.

A notable example was reported by Wu et al.^[72], who constructed a “dual-engine-driven” (DED) catalytic system, denoted as 1.0%FeMn&[ZnCr&ZSM-5@SiO₂]. This bifunctional configuration efficiently converts syngas into PX-rich aromatics via synchronized olefin and methanol intermediate pathways. In this system, the FeMn component (olefin engine) selectively produces light olefins from syngas, while the ZnCr component (methanol engine) generates methanol and dimethyl ether (DME). These intermediates undergo synergistic reactions within the

ZSM-5@SiO₂ zeolite. Specifically, light olefins preferentially adsorbed on the zeolite acid sites, effectively suppressing the conventional methanol-to-olefin side reactions. The adsorbed olefins subsequently undergo aromatization to form benzene and toluene intermediates, which then react with methanol/DME acting as alkylating agents via methylation reactions, ultimately yielding PX as the target product. A critical aspect of this system is the precise spatial organization of the catalytic components. To facilitate efficient hydrogen transfer and rapid diffusion of methanol/DME, the ZnCr (methanol engine) must be in close proximity (nanoscale to submicron scale, ~1–2 μm) to the ZSM-5@SiO₂ zeolite. In contrast, the FeMn (olefin engine) requires a larger separation (micron to millimeter scale, ~640–2 mm) from the zeolite to prevent over-hydrogenation of the olefin intermediates. This deliberate spatial modulation optimizes the reaction environment by balancing intermediate diffusion and active-site accessibility, thereby minimizing undesired side reactions. DFT calculations and ¹³C-isotope labeling experiments provide further mechanistic insights. The presence of olefin intermediates significantly raises the energy barrier for the methanol-to-olefins side reaction, thereby inhibiting it, while simultaneously lowering the activation energy for the alkylation of benzene with methanol (Figure 6). Isotopic tracing confirmed that the aromatic ring primarily originates from olefin aromatization, whereas methanol predominantly participates in the final alkylation step (e.g., methylation of toluene to form PX). Through this synergistic mechanism, the DED catalytic system achieved a remarkable PX space-time yield of 36.1 g/(kg·h), demonstrating the potential of dual-intermediate strategies for high-efficiency aromatics synthesis.

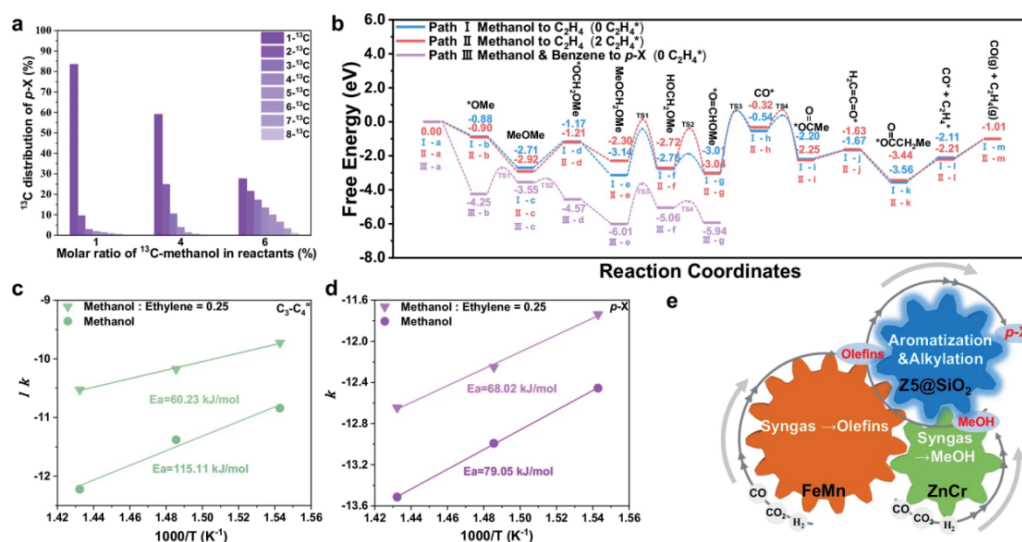


Fig. 6 The mechanism study of DED catalyst for PX synthesis from syngas^[72]
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4.4 Comparative analysis of reaction pathways: strengths, limitations, applicable conditions and scope

The selection of an appropriate reaction pathway is a critical determinant of catalytic performance, product distribution, and overall process economics in the direct conversion of syngas to PX-rich aromatics. The three principal pathways, utilizing olefin intermediates, methanol intermediates, or a dual-intermediate strategy each possess distinct characteristics, advantages, and limitations, making them suitable for different feedstock compositions, process objectives, and operating conditions. A systematic comparison of these pathways provides essential guidance for the rational design and industrial application of syngas-to-aromatics technologies.

The olefin intermediate pathway: The olefin intermediate pathway rooted in FTS, involves a two-step process. Syngas is first converted into C_2 – C_4 light olefins over Fe or Co-based catalysts. These olefins then diffuse to acidic zeolites (e.g., HZSM-5), where they undergo oligomerization, cyclization, and dehydrogenative aromatization to form aromatic products. The selectivity toward PX is primarily governed by the pore architecture and acidic properties of the zeolite^[74–77].

Strengths: This pathway typically achieves high CO conversion (>90%). When modified with promoters such as Mn, K, or Na, the selectivity to light olefins can reach 50%–60%, providing ample intermediates for subsequent aromatization^[78–79]. A key advantage is the minimal water-gas shift reaction activity, resulting in low CO_2 and methane selectivity, which enhances carbon atom economy. Furthermore, Fe-based catalysts exhibit strong resistance to sintering, ensuring sustained catalytic activity during prolonged operation.

Limitations: The product distribution is constrained by the Anderson-Schulz-Flory (ASF) model, generally limiting the maximum aromatic selectivity to below 50%. The strong acid sites of the zeolite can also promote the

formation of heavier aromatics, reducing the yield of desired BTX products.

Applicable Conditions and Scope: This pathway is well-suited for coal-derived syngas with an H_2/CO ratio of 1–2. In practice, physical mixing or layered bed configurations with zeolites are employed to prevent over-hydrogenation of olefin intermediates. It is primarily applicable for the co-production of mixed aromatics (BTX and C_{9+}) with high space-time yield. However, the relatively low PX selectivity and the associated high costs for downstream separation often limit its economic attractiveness, making it more suitable for integrated coal to olefins/aromatics complexes rather than dedicated, high-purity PX production.

The Methanol Intermediate Pathway: In contrast, the methanol intermediate pathway involves the initial conversion of syngas to methanol or dimethyl ether (DME) over metal oxide catalysts (e.g., ZnCrO_x , CuZnAl), followed by the transformation of these oxygenates into aromatics within the pores of a zeolite catalyst.

Strengths: The primary advantage of this route is the precise control over the aromatization pathway enabled by the zeolite's acidity and pore structure. This allows for high aromatic selectivity (70%–80%) and, through strategic modifications such as SiO_2 coating or Ga doping, the proportion of PX among xylenes can be tuned to exceed 70%.

Limitations: A significant bottleneck is the thermodynamic equilibrium of methanol synthesis, which typically restricts single-pass CO conversion to below 20%. There is also a substantial temperature mismatch between the optimal ranges for methanol synthesis (200–250 °C) and methanol-to-aromatics conversion (400–500 °C), necessitating complex reactor designs or multi-stage temperature control. Moreover, methanol and its intermediates are prone to causing coke deposition on the zeolite, leading to rapid catalyst deactivation and stability issues.

Applicable Conditions and Scope: This pathway requires syngas with a high H_2/CO ratio. It typically employs a tightly coupled system of metal oxides ($ZnCrO_x$, $CeZrO_x$) and modified HZSM-5 (e.g., core-shell $Z5@SiO_2$), operating at a compromised temperature of 350–450 °C to balance both reaction steps. It is best applied in scenarios demanding high-purity PX, such as the direct production of PX concentrates. However, the low per-pass CO conversion necessitates large reactor volumes and increases capital costs, rendering this pathway more suitable for small-scale modular units or processes integrated with CO_2 utilization.

The Dual-Intermediate (“Dual-Engine”) Pathway: To overcome the limitations of the single-pathway approaches, the “dual-engine” strategy has been developed, which synergistically combines FeMn-based (olefin engine) and ZnCr-based (methanol engine) catalysts^[73]. In this system, syngas is concurrently converted to both olefins and methanol, which then cooperate on the zeolite: olefins undergo initial aromatization to benzene/toluene, while methanol acts as an alkylating agent for the subsequent methylation step to form PX.

Strengths: This pathway offers a superior PX space-time yield (STY). For instance, the 1.0%FeMn&[ZnCr&ZSM-5@SiO₂] system has achieved a remarkable PX STY of 36.1 g/(kg·h), which is 4 to 8 times higher than that of single-pathway systems. The FeMn component ensures CO conversion above 50%, while the synergy between the ZnCr component and the zeolite maintains aromatic selectivity at 60%–70% and suppresses CO_2 selectivity to below 20%.

Limitations: The complexity of catalyst design is a major challenge. It requires precise spatial control over the catalyst components: the FeMn engine must be positioned at a micrometer-to-millimeter distance from the zeolite to prevent over-hydrogenation of olefins, whereas the ZnCr engine needs to be in nanoscale proximity to facilitate hydrogen species transfer. This makes catalyst preparation highly demanding. Additionally, the operating window is narrow, with strict requirements for temperature, pressure, and gas hourly space velocity (e.g., 375 °C, 5 MPa, 14400 mL/(g·h)) to maintain intermediate balance.

Applicable Conditions and Scope: This pathway demonstrates high adaptability to varying syngas H_2/CO ratios, making it compatible with both coal-based and biomass-derived feedstocks. It is implemented *via* physical mixtures or layered beds of FeMn, ZnCr, and modified zeolites, with optimized mass ratios to maximize synergy. Given its high PX STY and scalability, this pathway presents significant economic potential and is considered one of the most promising routes for large-scale industrial implementation of syngas-to-PX conversion.

5 Conclusion and outlook

The direct conversion of syngas to PX-rich aromatics represents a highly promising pathway for China to mitigate its heavy reliance on petroleum resources and achieve a

diversified supply chain for chemical feedstocks. This route aligns well with the nation’s energy structure characteristics, which are rich in coal but scarce in oil and supports its long-term sustainable development strategy. Despite significant progress in catalyst design and process understanding, several critical challenges continue to impede the industrialization of this technology, restricting its transition from laboratory-scale research to practical application.

5.1 Current challenges in catalyst performance and mechanistic understanding

From the perspective of catalyst performance, although certain catalytic systems have demonstrated excellence in specific metrics, such as high CO conversion or impressive aromatic selectivity, their comprehensive performance profile requires further improvement. A primary issue is the inherent difficulty in balancing high activity with long-term stability. During extended operation, catalysts are often prone to deactivation such as coke deposition and active metal sintering. For instance, Fe-based catalysts, while active for FTS, tend to form graphitic carbon under high-loading conditions, leading to a rapid decline in activity. Furthermore, although strategies like zeolite modification have succeeded in enhancing PX selectivity, the levels achieved often remain below the high threshold required for industrial economic viability. Many catalysts systems lack the ability to precisely steer the reaction pathway toward PX while simultaneously maintaining high overall aromatic selectivity. This results in complex product mixtures containing significant impurities, which subsequently entail high costs for separation and purification. Regarding the fundamental understanding of reaction mechanisms, while several pathways-such as those involving olefin intermediates, methanol intermediates, or a dual olefin-methanol mechanism-have been proposed, the dominant reaction channels and their interplay within a complex, working catalytic system are still not fully elucidated. This lack of deep mechanistic insight hinders the rational design of next-generation catalysts. Without a precise theoretical foundation, efforts to overcome performance bottlenecks remain largely empirical, making it challenging to fundamentally address issues of selectivity and stability.

5.2 Future research directions

To address these challenges, future research on catalysts for syngas-to-PX conversion should focus on the following key directions:

Precision Design of Catalytic Materials: Advanced synthesis and characterization techniques should be employed to achieve precise dispersion of active components within zeolite supports. The primary goals are to enhance metal-zeolite synergy and robustly inhibit deactivation pathways like coking and sintering. For

example, constructing core-shell zeolite structures or employing surface passivation can effectively suppress external acid-site-driven side reactions, thereby improving catalyst stability and PX selectivity.

Leveraging Data-Driven Approaches: The integration of machine learning (ML) and artificial intelligence (AI) presents a transformative opportunity for catalyst development. Machine learning algorithms can analyze vast datasets from experiments and high-throughput calculations to accurately predict key catalyst properties, including activity, selectivity, and stability. Furthermore, ML models can aid in optimizing the pore architecture and acid site distribution of zeolites, enabling the design of a zeolite environment with high shape selectivity tailored to the molecular dimensions of PX. AI technology can also simulate complex reaction networks, providing insights into the dominant reaction pathways and their interactions across different catalytic systems. This data-driven paradigm can significantly accelerate the discovery and optimization of catalysts, reduce development costs, and provide robust support for the eventual industrial application of syngas-to-PX technology.

Declaration of Competing Interest

The authors declare no conflict of interest.

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合成气制高选择性对二甲苯催化剂研究进展

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摘 要: 对二甲苯(PX)作为一种重要的化工原料, 对保障中国能源战略安全、推动化工产业向绿色低碳转型具有重要意义。本工作综述了近年来合成气直接制富含对二甲苯芳烃催化剂研究进展, 着重探讨了费托合成催化剂与分子筛耦合体系、甲醇合成催化剂与分子筛协同体系及双引擎驱动与分子筛催化体系。通过深入解析各类催化体系活性组分的电子结构特征、助剂协同作用机制以及分子筛孔道拓扑结构等关键要素, 揭示其对催化活性、选择性及稳定性的调控规律。同时, 基于反应中间体演变路径, 系统探究烯烃、甲醇及烯烃-甲醇双中间体反应机理, 阐述当前催化体系面临的活性与稳定性协同优化困难、PX定向选择性调控机制不明确等科学问题。基于上述问题, 对未来研究方向进行归纳总结。

关键词: 对二甲苯; 合成气; 费托合成; 甲醇; 反应机理

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