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Combined Strategies Enable Highly Selective Light Olefins and para-**Xylene Production on Single Catalyst Bed**

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catalytic cycle for the dominant generation of ethylene and, more importantly, enriches the methanol-to-hydrocarbons (MTH) chemistry and hydrocarbon pool mechanism. Furthermore, 0.4HZSM-5@S-1-CLD, an optimized HZSM-5 catalyst modified by the silicalite-1 epitaxial growth followed by silanization approach, realizes highly selective production of light olefins (especially ethylene) and para-xylene, while excellent reactant activity is maintained. This highly efficient coreaction route gives an important leading significance in synthesizing the raw materials for the polyolefin and polyester industries. The establishment of the combined control strategies provides a model for the joint production of multiple target chemicals in complex catalytic processes.

INTRODUCTION

Zeolite catalysis is a successful application of host-guest chemistry.¹ In the 1970s, zeolite acid catalysis and shapeselective catalysis were confirmed and successfully applied in the methanol-to-hydrocarbon (MTH) process. This important reaction in C1 chemistry realized the efficient conversion of methanol into hydrocarbons with high selectivity,^{2,3} which provided alternative ways to produce basic petrochemicals from nonoil resources, such as coal, natural gas, biomass, and so on.

Since ZSM-5 was invented, people have been pursuing the use of the Brönsted acidity and shape selectivity of ZSM-5 for the production of value-added hydrocarbon products, especially light olefins and aromatics with backbones in the chemical industry. For the development of MTH catalysts and technologies, the selective regulation of the products of this process has always been the focus of attention. The product distribution of methanol conversion over the zeolites with various topologies was significantly different.⁴⁻⁸ To rationally explain the influence of the topological structure on product selectivity, it was necessary to have a deep understanding of the reaction mechanism of the MTH process. In the 1990s, Dahl and Kolboe proposed the hydrocarbon pool (HCP) mechanism for methanol conversion, 9^{-11} and Olsbye et al. further proposed a dual-cycle mechanism based on the hydrocarbon pool mechanism; ethylene and propylene can be produced from the methylation and side-chain elimination of methylbenzene, while propylene and high alkenes are formed from alkene methylation and cracking route.^{12 -14} The different formation paths of ethylene and propylene indicated that adjusting the ratio of the two catalytic cycles might be a possible strategy for selectivity control. Based on the understanding of the MTH mechanism, researchers found that the influence of zeolite's topology on the product distribution of the MTH process is not only due to the shape-selective effect on the product but also closely related to the role of reactive HCP species, which are formed and retained in the zeolite. $^{4,5,15-17}$

Received: October 30, 2023 **Revised:** March 1, 2024 Accepted: March 1, 2024 Published: March 13, 2024



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Figure 1. Combined strategies provide a technical solution for the synthesis of basic raw materials of the polyolefin and polyester industries.

ZSM-5 and SAPO-34 have been proven to be successful catalysts in the MTH industry,¹⁸⁻²⁰ but in the MTH reaction, the two catalysts differ greatly in product generation and distribution. By the catalysis of the zeolite with MFI topology and 10-membered ring channels, the hydrocarbon products of MTH reaction over HZSM-5 are distributed in a wild range, including ethylene, propylene, higher olefins, aromatics, and alkanes (see Figure S1a).^{21,22} This is different from the shapeselective production of ethylene and propylene over SAPO-34 with an 8-membered ring window and CHA cavity (see Figure S1b).^{23,24} The different performance between ZSM-5 and SAPO-34 in MTH reaction originated from the zeolite topology.^{4,5,25} Since the pore size of HZSM-5 was close to the dynamic diameter of the benzene ring, modified ZSM-5 catalysts can work as the methanol to aromatics (MTA) catalyst and catalyze the shape-selective production of aromatics.^{26 -28} The external surface modification of HZSM-5 could improve the shape-selectivity in aromatic products, especially xylene, but this also caused the mass transfer reduction of reactants and products and thus the decrease in conversion rate to some extent.²⁹⁻³¹

Researchers have made many attempts to regulate the reaction products of methanol conversion catalyzed by HZSM-5. Adjusting the operating conditions could modulate the molar ratio of propylene and ethylene (P/E).^{32,33} Changing the diffusion properties or the density and strength of the acid center by modifying the catalyst could also vary the product distribution.^{34,35} In addition, some efforts have been made by cofeeding some species for the achievement of specially required product generation. Cofeeding acetaldehyde with dimethyl ether and methanol was investigated by Bhan and coworkers, and it was found that cofed-acetaldehyde could enhance ethylene selectivity by increasing the production of aromatics inside the zeolite pores, which enhanced the propagation of the aromatic-based catalytic cycle and resulted in the improvement of ethylene production.³⁶ Cofeeding water could suppress the hydrogen transfer reactions, especially that of propylene, which would improve the yield of light olefins and partially suppress the formation of aromatics and coke.^{37,38} More directly, cofeeding olefins or aromatics were applied to alter the composition of the hydrocarbon pool species and therefore varied the catalytic consequences of MTH product selectivity on HZSM-5.39

Although the research efforts have been paid off by some achievements in adjusting the selective production of the target products over the HZSM-5 catalyst, the implementation of some modification strategies is still far from completely satisfactory for the efficient utilization of raw materials and the acquisition of specially demanded products. To make the required reaction pathway dominant in the complex reaction network and shape-selective catalysis as much as possible, combined and synergistic strategies have been considered for both the zeolite material and zeolite catalysis. In this work, combined steering strategies were developed and applied to the methanol-toluene coreaction system (Figure 1). Cofeeding toluene steered the reaction route of methanol conversion, and ethylene can be produced as the main olefin product. At the same time, thin layers of silicalite-1 and silicon oxide were successively coated over the external surface of ZSM-5 by epitaxial growth and the chemical liquid deposition (CLD) methods, respectively, for shape-selective production of paraxylene among the aromatic products. By the aid of multiple techniques, such as diffusion analysis, in situ UV-Raman spectroscopy, and isotope labeling approaches, the studies revealed that cofeeding toluene introduces additional aromatic hydrocarbon pool species, making the pathway predominance of aromatic-induced ethylene production. The optimized modification of HZSM-5 ensures the reaction efficiency and shape selectivity, so high methanol-toluene conversion and shape-selective catalysis for light olefins and para-xylene can be realized at the same time on a single catalyst bed of HZSM-5@ S-1-CLD. The control strategy combining reaction pathway modulation and shape-selective catalysis provides a model of advanced technical solutions for the synthesis of basic raw materials for the polyolefin and polyester industries.

RESULTS AND DISCUSSION

Cofeeding Reaction of Methanol and Toluene on Single HZSM-5 Catalyst Bed for Optimized Production of Olefins and Xylenes. Principally, the production of valueadded olefins and aromatics (especially *para*-xylene) is achieved separately through different catalytic processes.^{42–45} In the present work, based on the understanding of the MTH reaction pathway and shape-selective catalysis over HZSM-5 (see Figures S1 and S2 and related notes), the cofeeding reaction of methanol and toluene is carried out in a ZSM-5-



Figure 2. Product distribution and in situ UV-Raman spectra for methanol-toluene coreactions. (a and b) Product distribution of the aromatics (a), and C_1 to C_6 products (b) with varied feed ratios of methanol to toluene. C_{9+} is the sum of aromatic products higher than xylenes. C_4 , C_5 , and C_6 in the legend are the sum of the alkene and alkane products. Catalysts: HZSM-5 (Si/Al = 66), 50 mg. WHSV: 2 h⁻¹. Reaction temperature: 733 K. (c and d) In situ UV-Raman spectra of coreactions of ¹²C-methanol with ¹²C-toluene (c), and ¹³C-methanol with ¹²C-toluene (d) with varied feed ratios of methanol to toluene. The Raman intensity was normalized with the characteristic peak of N₂ at 2331 cm⁻¹.

catalyzed reaction system for the production of light olefins and *para*-xylene on single HZSM-5 catalyst bed.

Methanol and toluene with varied ratios were cofed to the HZSM-5 catalyst bed. Methanol conversion remains at 100% under all reaction conditions, while toluene conversion varies with the cofeeding ratio. As the methanol/toluene ratio (M/T)varies from 10 to 0.5 with a constant total weight hour space velocity (WHSV) of 2 h⁻¹, toluene conversion gradually increases from 18.3% to 83.0% (see Figure S3), and the fraction of aromatic products is improved from 24.8% to 94.0% among hydrocarbon products (see Table S4). Figure 2a shows the product distribution of the aromatics. When toluene is cofed in methanol conversion, the benzene fraction decreases rapidly from 8.3% to less than 1%, and ethylbenzene is almost undetectable. As M/T varies from 10 to 0.5, the xylene fraction increases from 69.3% to 87.4% with a constant isomer proportion. The xylenes selectivity among hydrocarbon products shows a more pronounced increase, 17.2% under the feed ratio of M/T = 10, and 82.1% under the feed ratio of M/T = 0.5 (see Figure S3). It is noteworthy that there is an optimal yield of aromatic products (53%) under the feed ratio of M/T = 2 (marked with purple in Figure 2a). For the

distribution of C_1-C_6 chain hydrocarbons, as is shown in Figure 2b, methanol conversion without toluene cofeeding generates ethylene, propylene, and butenes as the main products, and their total selectivity is over 80%. Among them, propylene is the dominant product, and butenes are also produced in large amounts. When toluene is cofed, the proportions of specific hydrocarbon products change significantly. When cofeeding toluene with increasing proportion, it is surprisingly found that the selectivity of ethylene is greatly improved. For methanol conversion, generated ethylene accounts for 10.5% of C_1-C_6 aliphatic hydrocarbons. Increasing the proportion of cofed toluene (M/T from 10 to 0.5), the selectivity of ethylene is enhanced from 14.8% to 56.4%, and the ratio of ethylene/propylene (E/P) improves from 0.3 to 2.1. Compared to ethylene, the production of propylene and butenes is greatly depressed with toluene cofeeding together with xylene and other aromatics formation in the reaction. The cofeeding of toluene significantly modulates the production of light olefins and increases the E/P ratio, implying the regulation of the dominant reaction pathways of the cofeeding system for ethylene or propylene generation.



Figure 3. Isotopic labeling methanol-toluene coreactions for reaction mechanism. (a and b) Isotopic distribution of ethylene (a) and *para*-xylene (b) under varied feeding ratios at 20 min on stream. Catalysts: HZSM-5, 50 mg. WHSV: $2 h^{-1}$. Reaction temperature: 733 K. (c) Ethylene and *para*-xylene formation via MTH autocatalysis and via proposed side chain alkylation route and paring route in cofeeding reaction with ¹³C labeling.

The formation of olefins in methanol conversion comes from the reaction of methanol with olefinic and aromatic hydrocarbon pool species which acted as reaction intermediates. In situ UV-Raman spectroscopy was conducted to detect cofed toluene and the generated aromatic carbenium intermediates and investigate their role in the cofeeding reaction system. For the reaction of methanol, the peak at 1605 cm⁻¹, ascribed to the ring CC stretching vibration band of methylbenzenium cations (MB⁺),^{46,47} can be detected after 2 min on stream (Figure 2c). These organics work as the cocatalyst for methanol conversion according to the HCP mechanism.⁴⁸ The ring CC stretching vibration band of MB⁺ at 1605 cm⁻¹ has the strongest intensity for M/T = 2, which is well related to the aromatic yield results (Figure 2a) and suggests an optimized feed ratio for the cofeeding reaction. In situ UV-Raman technique of coreactions of ¹³C-methanol with ¹²C-toluene was employed to reveal the formation of the MB⁺ with different feed ratios (Figure 2d). For the reaction of ¹³Cmethanol, where there are no ¹²C atoms in the system, the peak at 1558 $\rm cm^{-1}$ is ascribed to the $^{13}\rm C^{13}\rm C$ stretching vibration band of ¹³C-MB⁺. As ¹²C-toluene is introduced into the system, the peak at 1605 cm⁻¹ appears again, which reveals

the contribution of toluene for the MB^+ formation as the critical aromatic hydrocarbon pool species. The Raman shift region between 1558 and 1605 cm⁻¹ in the cofeeding system is assigned to the vibration of MB^+ consisting of ¹³C and ¹²C, which is from the coreaction of ¹³C-methanol and ¹²C-toluene in the cofeeding reaction system and beneficial under M/T = 2. These results indicate that cofeeding toluene with methanol gives rise to the enhanced participation of the aromatic hydrocarbon pool species, and therefore, the aromatic-based reaction pathway will be predominantly reinforced.

Revealing the Reaction Pathways for Light Olefins and Xylene Production in Methanol–Toluene Cofeeding System. Considering the complex reaction network of coreaction of methanol and toluene (Scheme S1), the olefinic or aromatic hydrocarbon products not only come from the coreaction but also possibly from the independent MTO reaction. For the deduction of the exact reaction pathways, coreactions of ¹³C-methanol and ¹²C-toluene with variable methanol to toluene feeding ratio (M/T = 10, 5, 2, 1, and 0.5, in mole) were conducted, and the participation of ¹³C atoms from methanol and ¹²C atoms from toluene in the reaction was



Figure 4. Proposal of methanol-toluene coreaction pathways. (a) Critical intermediates capture and identification by GC-MS. (b) The catalytic routes of ethylene and xylene formation from the coreaction of methanol and toluene on HZSM-5. Calculated free energy barriers at 733 K are given in kJ/mol.

evaluated based on the isotopic distribution of the products at 20 min on stream.

The total ¹³C contents result (Figure S4) suggests that propylene and higher olefins are mainly derived from independent ¹³C-methanol conversion at a high M/T ratio, while the cofed ¹²C-toluene contributes more to ethylene formation even though toluene makes up only a minor portion of the cofeeding raw materials. When toluene accounts for a larger fraction of the cofeeding system with low ¹³Cmethanol/¹²C-toluene cofeeding ratios (M/T = 2, 1, and 0.5), a considerable amount of ¹²C atoms would also be introduced into propylene and higher olefins, which indicates that the cofed ¹²C-toluene may also participate the formation of propylene and higher olefins to some extent.

According to the isotopic distribution of ethylene shown in Figure 3a, ${}^{13}CH_2 = {}^{13}CH_2$ is the main product under high M/T ratios, indicating that ethylene mainly comes from the

independent ¹³C-methanol conversion. But for the case of higher toluene proportion, ¹³CH₂=¹²CH₂ appears as the main species. For all cofeeding reactions, ¹²C-ethylene (¹²CH₂=¹²CH₂) is detected, and its proportion increases from 2% to 20% with the increase of cofed ¹²C-toluene. The proposed routes for ethylene generation in the cofeeding system are shown in Figure 3c. For the MTH reaction following the aromatic-based HCP reaction route, side chain alkylation and elimination reactions account for ¹³CH₂=¹²CH₂ generation. In parallel, the coreaction of methanol and cofed toluene with the contraction and expansion of the benzene ring results in the formation of ¹²C-ethylene (¹²CH₂=¹²CH₂).

Among the aromatic hydrocarbon products in the cofeeding system, xylenes appear as the main product. Taking *para*-xylene as an example, most of *para*-xylene is mono ¹³C-labeled

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Figure 5. Enable the predominant production of light olefins and xylenes via cofeeding reaction.

in all the cofeeding reactions, and the proportion exceeds 80% under the feed ratio of M/T = 0.5 (Figure 3b), indicating that the mono ¹³C-labeled *para*-xylene is mainly produced by the direct methylation of ¹²C-toluene with ¹³C-methanol. Furthermore, there is still a considerable proportion of *para*-xylene with bis- or tris-¹³C labeled under different cofeeding ratios. The generation of *para*-xylene with more than one ¹³C atom incorporation indicates the occurrence of methanol conversion to xylene reactions or some other possibilities in the complicated network, such as benzene ring contraction and expansion in the cofeeding reactions.

The application ¹³C-labeling technique in the coreactions of ¹³C-methanol and ¹²C-toluene helps to deduce the detailed and exact reaction pathways. Based on the above results, besides the MTH autocatalysis, a coreaction side chain alkylation route and paring route for ethylene and *para*-xylene formation are proposed and given in Figure 3c, which are perfectly matched with the isotope distribution. As a result of toluene participation, these proposed coreaction routes are distinguishable from the side-chain mechanism and paring mechanism for the MTO process, which are guided by intermediate aromatic species containing more substituted methyl groups and claim that the side-chain mechanism leads to the formation of ethylene, and the paring mechanism mainly forms propylene or isobutene.^{49,50}

According to the evidence from isotope labeling reactions of ¹³C-methanol with ¹²C-toluene, the reaction paths are proposed in detail (see Figure S6). To capture the key reaction intermediate species linking the coreaction of methanol and toluene to the production of ethylene and xylene, a trace amount of toluene is cofed with methanol on HZSM-5 to prevent some hard-to-detect surface organic species from being masked in the chromatogram. As is shown in Figure 4a, by employing the FFAP column to directly separate the effluents of the coreaction, at the retention time of 3-8 min, besides toluene, xylenes, and ethylbenzene, two peaks with m/z = 94 attributed to dimethylcyclopentadiene are also detected. Surprisingly, together with the above-mentioned species, a very weak peak at 3.38 min, which has the same

molecular weight as toluene but a different retention time is captured. In addition, another two peaks (retention times at 5.18 and 5.33 min) are also detected between the peaks of ethylbenzene and para-xylene. Since toluene has no other isomers with benzene rings, and all the phenyl isomers of xylene (ethylbenzene, para-, meta-, and ortho-xylene) are detected, the peak at 3.38 min with m/z = 91 is assigned to methylenecyclohexadiene (M⁼CH⁼⁼) or methylmethylenecyclopentadiene (MM⁼CP⁼⁼), and the other two peaks at 5.18 and 5.33 min with m/z = 106 are assigned to two other methylenecyclodiene species, methylmethylenecyclohexadiene (MM⁼CH⁼⁼) or dimethylmethylenecyclopentadiene (di-MM⁼CP⁼⁼). Even though they are predicted as the very important intermediates in the reaction cycle of ethylene or propylene generation from methanol conversion,^{51,52} due to their high reactivity, the capture and identification of them are unprecedented.

Based on the capture of the MM⁼CH⁼⁼ and di-MM⁼CP⁼⁼ in the coreaction of methanol with toluene, two routes involving these two key intermediates for ethylene formation are established and shown in Figure 4b, and density functional theory (DFT) calculations are used to assess the feasibility and the contribution of these routes from an energetic point of view. Computational details are provided in Figure S7 and the "Theoretical Calculation" section in the Supporting Information for the supplemental experimental procedures.

Both routes start from the methylation reaction (1) of toluene with methanol to form 1,4-dimethylbenzenium cation (1,4-diMB⁺) over the Brönsted acid site. Subsequently, in route A, the following deprotonation (2A) of 1,4-diMB⁺ produces $MM^{=}CH^{==}$ with an exocyclic double bond, which is directly captured and is identified in Figure 4a. Then $MM^{=}CH^{==}$ methylation with methanol forms 4-methyl-ethylbenzenium with ethyl side-chain (3A). Furthermore, 4-methyl-4-ethylbenzenium, after the hydride transfer (4A–6A) steps, can eliminate the ethyl group to generate ethylene (7A). In route A, the free energy barriers for the two methylation steps (1, 3A) catalyzed by HZSM-5 are 136.6 and 104.3 kJ/mol, respectively. The deprotonation reaction (2A) is a facile step,



Figure 6. Combined strategies to achieve highly efficient production of light olefins and *para*-xylene over modified HZSM-5. (a) Schematic representation of the modification processes. (b–e) SEM images and EDS mapping of compositional distributions of Al of HZSM-5 samples: HZSM-5 (b), HZSM-5-CLD (c), 0.4HZSM-5@S-1 (d), and 0.4HZSM-5@S-1-CLD (e). (f, g) TEM images of modified HZSM-5: HZSM-5-CLD (f), 0.4HZSM-5@S-1-CLD (g). (h) Comparison of target product selectivity and toluene conversion over HZSM-5 before and after modification. Catalysts weight: 50 mg. WHSV: 2 h⁻¹. Reaction temperature: 733 K. Time on stream: 20 min. (i) IR spectra of the four ZSM-5 samples after 2,6-di*tert*-butylpyridine adsorption and desorption at 423 K. (j) Comparison of the D/R^2 of the products over HZSM-5 and 0.4HZSM-5@S-1-CLD. (k) Catalytic performance after applying different strategies.

with a free energy barrier of 61.5 kJ/mol. The hydride transfer (4A–6A) and ethylene elimination reactions (7A) are more energetically feasible with free energy barriers between 16.8 and 99.8 kJ/mol.

Based on the observation of MM⁼CP⁼⁼ and di-MM⁼CP⁼⁼, the formation of ethylene from the pairing route is predicted as

route B and evaluated. Starting from 1,4-diMB⁺, 2, 5dimethylbicyclo-[3.1.0] hexenyl cation is formed via the step of ring contraction (2B), followed by ethylene elimination (3B) to produce 1-methlycyclopentadienyl cation. This cation can deprotonate (4B) to form methylenecyclopentadiene (M⁼CP⁼⁼). It is noteworthy that this critical intermediate can go through methylation with methanol (**5B1**, **10B**, Figure S8), deprotonation and protonation to produce di-MM⁼CP⁼⁼, tri-MM⁼CP⁼⁼ (for complete process see Figure S8), and their corresponding cations (**6B**). Finally, the reaction route is fulfilled after hydride transfer (**7B**), ring expansion (**8B**), and deprotonation reactions (**9B**). The ring contraction step (**2B**) has to overcome a relatively high free energy barrier of 170.7 kJ/mol in route B with a paring mechanism. The M⁼CP⁼⁼ undergoes a successive methylation process to form poly-MM⁼CP⁼⁼ with a free energy barrier of 120.5 and 119.0 kJ/mol. The deprotonation and protonation reactions (**4B**, **9B**) are facile steps with free energy barriers of 7.8–8.03 kJ/mol.

The theoretical evaluation of side-chain and pairing catalytic cycles for the ethylene formation suggests that these two reaction routes can both induce ethylene formation, in which toluene, polymethylbenzene, MM⁼CH⁼⁼, and poly-MM⁼CP⁼⁼ play significant roles in ethylene formation as the critical intermediates. The side chain reaction pathway (route A) is a more feasible reaction pathway for ethylene generation due to its lower reaction energy barrier. At the same time, xylene can be successfully generated through the toluene methylation and deprotonation over the Brönsted acid center. The feasibility of the reaction route corresponds well with the coreaction routes revealed by the isotopic labeling technique (Figures 3c and S6).

The complete reaction network of the cofeeding reaction system is summarized in Figure 5. The coreaction of toluene and methanol not only generates the target product of xylene but also generates key hydrocarbon pool species, consisting of polymethylbenzene, MM⁼CH⁼⁼, MM⁼CP⁼⁼ species, and their corresponding cations, which greatly promote the production of light olefins, especially ethylene. The establishment of the coreaction network reveals a new state of hydrocarbon pool mechanism under the condition of aromatic cofeeding, which is an extension of that in the conventional MTO process. It also reveals the key factor leading to the loss of shape-selectivity for aromatics in the coreaction process over HZSM-5 zeolite, i.e., the side reactions occurrence over the external surface including isomerization, alkylation, and disproportionation.

Modifying HZSM-5 for Shape-Selective Production of para-Xylene and Ethylene. The cofeeding reaction of methanol and toluene can effectively and selectively produce light olefins and xylene over HZSM-5. In principle, the difference in intracrystalline diffusion properties in HZSM-5 can enable the shape selectivity of para-xylene among the products due to the advantages of para-xylene in terms of diffusion among xylene isomers and other C₉₊ aromatics (see Figure S2b and related notes). However, selective para-xylene production cannot be achieved over unmodified HZSM-5. A series of side reactions occur over the external surface of HZSM-5 without the confined effect of the 10-membered ring channels, resulting in an unsatisfactory product distribution of aromatics rather than producing the most desired and valueadded product, para-xylene.53-55 Therefore, to achieve the highly selective production of light olefins and para-xylene simultaneously, side reactions need to be suppressed or even prohibited.

To suppress the side reactions (alkylation, isomerization, and disproportionation) occurring at the acidic sites on the outer surface of HZSM-5, $^{56-58}$ the chemical liquid deposition (CLD) method is adopted and applied by using tetraethylor-thosilicate (TEOS) with a larger kinetic diameter (1.03 nm)

than the pore dimension of HZSM-5 to cover the outer surface acid sites.⁵⁹ In this way, the *para-xy*lene selectivity is enhanced from 26.9% to 92.6% (among xylenes; Figure 6h), and C₉₊ selectivity decreases significantly from 15.5% to 2.3% (Table S5), indicating that the external surface reactions have been effectively inhibited. However, toluene conversion over HZSM-5-CLD (31.3%) decreased significantly compared to that over the unmodified HZSM-5 (68.4%). One immediate reason is that the deposition of silica at the pore openings leads to a certain extend of pore coverage or size reduction, which increases diffusion limitation and reduces the accessibility of toluene to the acid sites within the catalyst channels. Over HZSM-5-CLD, when the selectivity of product *para-xy*lene is enhanced, the conversion of toluene cannot be well maintained.

The epitaxial growth of silicalite-1 (S-1) is an effective means to achieve a nonacidic external surface. However, excessively thick S-1 layer lead to a substantial increase in crystal size, which elongates the diffusion paths for both the reactants and products. Though a significant enhancement in product selectivity would be achieved, an increase in crystal size also results in a noticeable decrease in reactant conversion due to the increased diffusion limitations (Figure S9). Thinlayered growth of the S-1 can be achieved by reducing the amount of silicon source or adding alcohols as a growth inhibitor, which can enhance product selectivity without the cost of reactant conversion. $^{60-63}$ But only epitaxial growth modification usually cannot achieve advantageous selectivity for para-xylene. To address these issues, an optimized joint modification strategy, including thin-layer epitaxial growth of S-1 and a further CLD process, is employed to achieve high reactant conversion and high para selectivity simultaneously. A series of mHZSM-5@S-1 have been synthesized by hydrothermal method to realize the epitaxial growth of S-1 layers on the external surface of HZSM-5, and the S-1 lavers are adjusted by the ratio of HZSM-5 to the starting gel, where *m* represents the mass ratio of HZSM-5 to SiO₂ for synthesis. The epitaxial growth of S-1 promotes para-xylene selectivity, while the conversion of toluene is maintained at a high level (Figure 6h). On the obtained *m*HZSM-5@S-1 catalyst, when *m* is set at 0.2, the para-xylene selectivity (among xylenes) increases from 26.9% over HZSM-5 to 89.7% (Table S6). The epitaxial growth process has built an MFI crystal structure that allows effective diffusion of toluene for conversion. Based on the epitaxial growth of S-1, the further sight silanization treatment with the CLD method for the S-1 layer achieves a more completely nonacidic external surface for the highly selective production of para-xylene among xylene isomers and other aromatic products. The thickness of the amorphous silanization deposit by the CLD method over HZSM-5 is above 13 nm (Figure 6f), while that over the S-1 layer (Figure 6g) is much thinner. The nonacidic external surface constructed by the epitaxial growth of S-1 inhibits the excessive deposition of amorphous silica. Further slight silanization only fills the defect position of the S-1, which avoids the blockage of the pore window. In this way, high selectivity can be also realized without the cost of reactivity of the catalyst. Over 0.4HZSM-5@S-1-CLD, an optimized catalytic performance is achieved, with nearly 100% methanol conversion and 45% toluene conversion, the total selectivity of valuable products (light olefins and para-xylene) is achieved by 90.0%, and especially, ethylene production accounts for 53.6% of light olefins, and

para-xylene production accounts for 94.0% of xylene products (Figure 6h and Table S5).

Using 2,6-ditert-butylpyridine (dTBPy) as the probe molecular,⁶⁴ the external surface acidity of the modified HZSM-5 catalysts was determined by infrared spectroscopy (Figure 6i). Compared with HZSM-5, the modified catalyst HZSM-5-CLD by CLD-silanization of the HZSM-5 external surface and HZSM-5@S-1 obtained by epitaxial growth of S-1 on HZSM-5 can cover the acid sites of the external surface to a certain extent. Optimizely, using a joint external surface modification strategy, S-1 epitaxial growth by hydrothermal crystallization combined with silica deposition by CLD over HZSM-5 (0.4HZSM-5@S-1-CLD) almost completely eliminates the acid sites on the external surface and effectively inhibits the generation of xylene isomers and C_{9+} aromatics from the secondary reactions catalyzed by the acidic sites on the external surface.

Interestingly, the evaluation of the diffusion behavior of the guest molecule in the zeolite catalyst indicates that the catalyst modifications performed in this work bring about the diversified diffusion properties $(D/R^2$ value, given in Figure 6j, obtained by fitting the desorption curves given in Figure S10). Compared with HZSM-5, the D/R^2 values of ethylene, propylene, and *n*-butene are significantly enhanced on the 0.4HZSM-5@S-1-CLD. The D/R^2 value of toluene and paraxylene remains at the same level or slightly higher than that of HZSM-5 without modification. The repair of crystal defects and the coverage of external surface acid sites during epitaxial growth and silica deposition would weaken the surface barrier resistance and improve the diffusion property of ethylene, propylene, n-butene, and para-xylene,⁵⁶ which helps the selective formation of light olefins and para-xylene. At the same time, toluene conversion can be maintained at a high level. Also in this way, the light olefins could leave the zeolite pores as soon as possible, and the occurrence of side reactions of these products can be suppressed. On one hand, the secondary reactions to form xylene isomers, such as orthoxylene and meta-xylene, in the coreaction of methanol and toluene are depressed with the external surface acid site elimination by catalyst modification; on the other hand, the increased diffusion restriction of the byproducts of xylene isomers and large aromatics in the modified catalyst 0.4HZSM-5@S-1-CLD gives rise to shape-selective catalysis for paraxylene among aromatic products. The differentiated diffusion performance after catalyst modification thereby ensures the high selectivity of target products, together with high reaction efficiency.

The schematic representation of the modification processes is given in Figure 6a based on the catalytic tests and SEM results (Figure 6b-e). As indicated in this study (Figure 5), light olefins and xylene can be predominantly produced from the reaction network of the methanol/toluene cofeeding system. Toluene cofeeding improves methanol conversion to light olefins due to the participation of cofed toluene and produced aromatic products into the reaction route as hydrocarbon pool species for olefin generation. The improved aromatic-based cycle gives rise to improved olefins production (especially for ethylene production over HZSM-5, E/P achieved 1.0 under M/T = 2). As the inhibition of the reactions on the external surface with catalyst modification, the coreaction of methanol and toluene over HZSM-5@S-1-CLD can only occur inside the HZSM-5 grain. The shape-selective catalysis by the diffusion restriction is highlighted and takes

effect in the reaction for para-xylene production. Shapeselective production for value-added aromatic has been realized. Among hydrocarbon products, the para-xylene fraction increases from 14.7% over HZSM-5 to 63.3% over 0.4HZSM-5@S-1-CLD, and the proportion of para-xylene among xylenes increases from 26.9% to 94.0% (Figure 6k). It is noteworthy that the toluene conversion over 0.4HZSM-5@S-1-CLD keeps well and remains at 45%, which is much higher than that of HZSM-5-CLD. In comparison to previous reports, the joint modification strategy in this study demonstrates a clear advantage in terms of simultaneous achievement in maintaining relatively high reactant conversion while achieving an excellent para selectivity for xylene (Figure S11 and Table S7). Cofeeding methanol-toluene is cofed over HZSM-5@S-1-CLD, the methanol conversion rate remains 100%, and the selectivity of light olefins $(C_2^{=}:C_3^{=}:C_4^{=} = 54:34:12)$ reaches 89.6% among aliphatic hydrocarbons. Ethylene production has been further promoted (E/P increases from 1.0 to 1.6 under M/T = 2). Efficient and shape-selective production of light olefins and para-xylene has been successfully achieved simultaneously by employing combined strategies in a methanol-toluene cofeeding reaction system over a modified HZSM-5 catalyst.

CONCLUSIONS

Zeolite-catalyzed methanol-toluene cofeeding reaction enables an applicable process for the simultaneous production of light olefins and *para*-xylene. The combined strategies including reaction pathway guidance and zeolite shapeselective catalysis ensured high selectivity to light olefins and *para*-xylene over the modified HZSM-5 catalyst.

A complete reaction network of the methanol/toluene conversion system has been established. Cofeeding toluene can break the stable product distribution of the MTH process on HZSM-5, leading the olefin product distribution to tilt toward ethylene production. Isotopic labeling experiments confirm that cofeeding reactive aromatic hydrocarbon pool species intensifies the ethylene formation pathway in the reaction network, resulting in the enhanced ratio of ethylene to propylene from 0.2 of MTH to 1.0 of cofeeding reaction (M/T = 2). In situ UV-Raman spectroscopy demonstrates that cofeeding toluene promotes the formation and accumulation of methylbenzenium cations. Through the precise identification of critical intermediates, for the first time, the methylmethylenecyclodienes have been successfully captured and identified. Based on these findings, the catalytic cycle of ethylene production can be established and confirmed to be energetically favorable, in which the methylmethylenecyclopentadiene (MM⁻CP⁻⁻⁻), methylmethylenecyclohexadiene (MM⁻CH⁻⁻⁻), and methylbenzenes work as the key intermediates. These findings provide new evidence for the proposed hydrocarbon pool mechanism and expand our knowledge of carbocation chemistry in solid-acid catalysis.

Furthermore, together with the highly selective production of light olefins, a joint modification strategy is employed to improve the selectivity of *para*-xylene in the cofeeding reaction of methanol and toluene. The silicalite-1 epitaxial growth and CLD-silanization approaches jointly performed over HZSM-5 realize the coverage of the Brönsted acid sites on the external surface to effectively inhibit the formation of aromatic byproducts (*meta*, *ortho*-xylene, and C_{9+} aromatics) from side reactions such as alkylation, isomerization, and disproportionation occurred on the external surface. With these modifications, the catalyst presents optimal reactant and product shape selectivity by enhancing the diffusion properties of light olefins, toluene, and *para*-xylene and suppressing that of other xylene isomers, and the high reactivity of methanol and toluene can be maintained. On 0.4HZSM-5@S-1-CLD, high selectivity to light olefins (ethylene, propylene, and butene account for 89.6% of C_1-C_6 hydrocarbons) and high selectivity to *para*-xylene production (94.0% among the xylene isomers) have been achieved, and the total selectivity of light olefins and *para*-xylene accounts for 90%. At the same time, excellent catalytic activity has been maintained (100% methanol conversion and 45% toluene conversion).

Therefore, by precisely strengthening or inhibiting certain paths in the complicated reaction network, highly efficient coproduction of value-added products, such as light olefins (mainly ethylene) and *para*-xylene, can be achieved over a modified zeolite catalyst. This will provide new applicable production routes for the required reaction materials in the plastic and polyester industry and also supply useful solutions for combined modulation in complex reaction systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c12087.

Supplemental experimental procedures, MTH performance (Figure S1); acid catalysis and shape-selective catalysis of HZSM-5 (Figure S2); toluene conversion and xylene selectivity (Figure S3); total ¹³C content of main products under varied feeding ratios at 20 min on stream (Figure S4); isotopic distribution of aliphatic hydrocarbon products (Figure S5); proposed coreaction pathways for ethylene and para-xylene production (Figure S6); representation of HZSM-5 framework structures by 72T cluster models (Figure S7); the complete process of 5B1/5B2 of route B in Figure 4b (Figure S8); xylene distribution and toluene conversion of HZSM-5 zeolites with different crystal sizes and zeolites after surface modification (Figure S9); ZLC desorption curves (Figure S10); plots of para-xylene selectivity against toluene conversion on modified catalysts (Figure S11); proposed reaction network for coreaction of methanol and toluene (Scheme S1); methanol conversion and product distribution over HZSM-5 (Table S1), SAPO-34 (Table S2); the projected diameter of the molecule on the three principal axes of inertia and their diffusional time constants over HZSM-5 before and after modification (Table S3); the conversion and product distribution of coreaction of methanol and toluene over HZSM-5 under varied feeding ratios (Table S4); catalytic performance of modified HZSM-5 catalysts: conversion and product distribution for coreaction of methanol with toluene (Table S5); the reactant conversion and product distribution of coreaction of methanol with toluene over HZSM-5 after coating with silicalite-1 and SiO₂ deposition by CLD method (Table S6); surface modification catalysts and their catalysis performance in previous reports (Table S7) (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (21991093, 21991092, 21991090, 22288101, 22172166), the Youth Innovation Promotion Association CAS (2021182), the Clean Combustion and Low-carbon Utilization of Coal, Strategic Priority Research Program of the Chinese Academy of Sciences (Grant no. XDA 29000000), and the Innovation Research Foundation of Dalian Institute of Chemical Physics, Chinese Academy of Sciences (DICP I202217) for the financial support. We thank Prof. Shutao Xu for the constructive discussion.

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