

Study on the coke deposition characteristics of hierarchical ZSM-5 zeolites with synergistic regulation of pore structure and temperature in benzene catalysis

ZENG Qingzhou¹, HAN Xuefeng², ZHAO Hongyu³, LI Jihui⁴, LIU Shucheng^{1,2,*}

¹ School of Mining, Liaoning Technical University, Fuxin 123000, China;

² Erdos Research Institute of Liaoning Technical University, Erdos 017004, China;

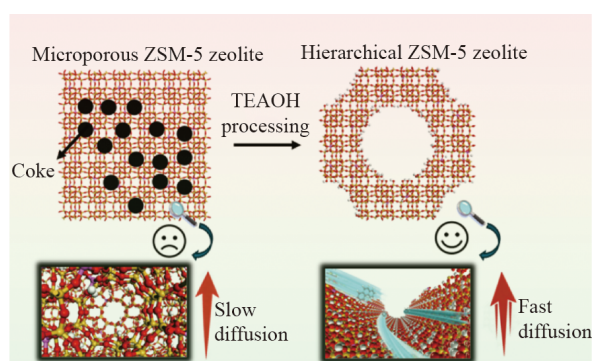
³ School of Resources and Safety Engineering, University of Science & Technology Beijing, Beijing 100083, China;

⁴ School of Chemical and Environmental Engineering, China University of Mining & Technology (Beijing), Beijing 100083, China

Abstract: Carbon deposition caused by mass transfer limitations is a key challenge for traditional microporous ZSM-5 zeolites in the process of coal tar catalytic cracking. To address this problem, benzene was selected and used as a model compound for coal tar in the study. The parent ZSM-5 (NL-ZSM-5) was modified with tetraethylammonium hydroxide (TEAOH) to prepare hierarchical ZSM-5 zeolites with different mesopore sizes. A suite of characterization techniques (XRD, FT-IR, BET, TEM) were combined with fixed-bed experiments and molecular simulations to systematically investigate the effects of pore structure, acidic properties, and reaction

temperature on the coking mechanism. The characterization results confirmed that mesopores were successfully introduced *via* the selective desilication with TEAOH, while the original MFI topological structure was retained. When TEAOH concentration is 0.4 mol/L (ZSM-5-C), the total pore volume increases from 0.24 to 0.43 cm³/g, and the amount of Brønsted acid (B acid) increased from 0.28 to 0.67 mmol/g. Moreover, the acid site accessibility was significantly improved. Analysis of catalytic experiments and carbon deposition indicate that carbon deposition is effectively inhibited in the hierarchical pore structure through a synergistic effect of “diffusion enhancement and adsorption-site regulation”. The coke amount of ZSM-5-C is 4.0%, which is only one-third of that of the pure microporous NL-ZSM-5 (11.9%). The results of molecular dynamics simulations confirm that the diffusion coefficient of benzene in the 3.0 nm mesopore model is an order of magnitude higher than that in the 2.0 nm model. Furthermore, the adsorption capacity decreases with the increasing in mesopore size, resulting in a shorter residence time of molecules within the pore channels. In addition, although increasing the temperature can enhance the molecular diffusion rate, it also exponentially intensifies surface condensation reactions (Arrhenius effect), which becomes the dominant driver of coke formation. The hierarchical pore structure, however, can effectively mitigate this negative effect. This research provide a theoretical basis for the design of high-efficiency and coke-resistant catalysts for coal tar conversion.

Key words: hierarchical porous ZSM-5 zeolite; TEAOH modification; catalytic conversion of benzene; carbon deposit regulation; molecular simulation (GCMC/MD)



As the by-product of coal pyrolysis, coal tar is rich in aromatic hydrocarbons such as benzene, toluene, and xylene (BTX). It serves as a crucial resource for the production of

high-value-added chemicals^[1-2]. Due to the complex composition of coal tar, there are significant challenges in directly investigating its molecular behavior. In recent

Received: 2025-10-26; Revised: 2025-12-05

Foundation items: Supported by a Basic Research Project of Liaoning Education Department (LJKZZ20220045, LJKMZ20220691) and National Science Foundation of China (52304290).

* Corresponding author. E-mail: lsc33884287@163.com.

DOI: 10.1016/S1872-5813(26)60653-6 CSTR: 32157.14.2097-213X.2026.JFCT.0008 Associated Data DOI: 10.57760/sciencedb.35311

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18725813>)

years, the use of representative coal tar model compounds to replace real coal tar has become an effective strategy for studying the conversion properties of coal tar^[3–5]. Among these, benzene is a monocyclic aromatic hydrocarbon with relatively high content in coal tar, and its molecular structure represents the simplest monocyclic conjugated configuration within the BTX system. The catalytic reaction pathways of benzene, such as alkylation and cracking, share commonalities with the conversion rules of other aromatic hydrocarbons in coal tar^[6]. Therefore, the selection of benzene as a model compound for coal tar—and the subsequent investigation of its molecular catalytic behavior—offers significant scientific value for advancing the high-value-added catalytic conversion of coal tar.

ZSM-5 zeolite, featuring a unique MFI topological structure (intersecting 10-membered ring micropores with a pore size of 0.53–0.56 nm), appropriate acid strength, and excellent hydrothermal stability, are widely utilized in aromatic hydrocarbon catalytic reaction systems^[7–9]. However, in the actual catalytic process, the traditional pure microporous ZSM-5 often faces serious carbon deposition problems. The kinetic diameter of the benzene molecule (about 0.59 nm) is close to that of the ZSM-5 microporous pore size, resulting in high mass transfer resistance and long retention time. At the same time, benzene and its alkylated derivatives are prone to sequential dehydrogenation and condensation reactions at strong acid sites. This process leads to the formation of polycyclic aromatic hydrocarbon (PAH) deposits, which block micropore channels and cover active sites, ultimately resulting in rapid catalyst deactivation^[10–12]. Therefore, how to regulate the pores and acidity characteristics of ZSM-5 through structural modification and inhibit the formation of carbon deposits have become a key scientific problem to improve its stability in coal tar conversion.

To address the mass transfer limitations inherent to microporous ZSM-5, the construction of a “microporous-mesoporous” hierarchical architecture has attracted considerable research interest^[13]. Currently, the synthesis of hierarchical ZSM-5 zeolites primarily involves hard-template, soft-template, and post-treatment methods^[14–16]. Among these, the alkali solution post-treatment method has attracted considerable attention due to its simplicity, cost-effectiveness, and ability to precisely control mesopore content. Tetraethylammonium hydroxide (TEAOH), a weakly basic modifier, selectively dissolves silicon species from the ZSM-5 framework, exhibiting a higher hydrolysis rate for Si–O–Si bonds compared to Si–O–Al bonds. This process introduces mesopores while maintaining the MFI topology^[17–18]. Previous research has demonstrated that TEAOH treatment enhances the external surface area and pore volume of ZSM-5, thereby improving molecular mass transfer efficiency. However, the structure-activity relationship involving “mesopore content-acid distribution-coking behavior,” particularly the adsorption-diffusion mechanisms at the molecular level, remains inadequately investigated. Specifically, it remains unclear whether the

introduction of mesopores influences the formation of carbon precursors by altering the number and distribution of acid sites, such as the migration of strong acid sites from micropore to mesoporous surfaces. Additionally, the synergistic regulation of molecular diffusion and surface reaction rates by reaction temperatures within multi-pored ZSM-5 has not been clearly elucidated. Furthermore, Conventional analyses of coking behavior have largely depended on macroscopic characterization (e.g., TG/DTG, BET), which fails to fundamentally elucidate how hierarchical pores suppress coking. Moreover, they lack molecular simulations that could reveal microscopic processes such as the density distribution and diffusion pathways of benzene molecules within pores.

Based on this, TEAOH was employed as a modifier in this study to prepare a series of hierarchical ZSM-5 molecular sieves by varying its concentration (0.20, 0.30, 0.40 mol/L). The evolution of crystal structure, pore characteristics, acid distribution, and catalytic performance in the modified samples was systematically examined. X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were employed to confirm the formation of the hierarchical structure and the integrity of the crystals. Brunauer-Emmett-Teller (BET) analysis and pyridine infrared spectroscopy (Py-IR) were utilized for the quantitative assessment of pore volume, specific surface area, and the number and types of acidic sites. Fixed-bed catalytic experiments were conducted to evaluate catalyst stability during benzene conversion, while thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were used to determine the amount and coke type. Concurrently, molecular simulations, including Grand Canonical Monte Carlo (GCMC) and Molecular Dynamics (MD), were employed to reveal microscopic-level insights into the adsorption isotherms, adsorption heats, and self-diffusion coefficients of benzene molecules within hierarchical pore models of varying aperture sizes. This elucidated the synergistic regulation mechanism of “pore structure-acidity-temperature” on coking behavior. This study aims to provide theoretical support for the design of multi-level porous molecular sieve catalysts with enhanced anti-coking properties, thereby advancing their practical application in the catalytic conversion of complex systems such as coal tar.

1 Experimental

1.1 Preparation of the parent ZSM-5

The preparation process of the parent zeolite was listed in Figure 1. Tetrachloroethyl orthosilicate (TEOS) serves as the silicon source, tetrapyridinium hydroxide ammonium (TPAOH) acts as the template agent, and aluminum isopropoxide (AIP) functions as the aluminum source.

Initially, TEOS was added dropwise to a pre-prepared TPAOH solution, maintaining a ratio of 1 TEOS: 0.025 AIP: 0.25 TPAOH: 40 H₂O, while stirring at 35 °C in a water bath for 3 h to produce a clear silica source sol. Concurrently, AIP was dissolved in deionized water and hydrolyzed thoroughly at 85 °C in a water bath for 1 h to generate the aluminum source solution. This aluminum source was then added dropwise to the silicon source sol, with stirring continued at 35 °C for 2 h to ensure complete mixing. Subsequently, the system was heated to 85 °C for a 3 h de-alcoholization treatment (ethanol/isopropanol evaporation). At the same time, the deionized water was added to maintain the initial liquid level. The resulting precursor colloid was transferred to a stainless steel crystallization vessel lined with polytetrafluoroethylene (PTFE) and subjected to static crystallization at 170 °C for 72 h. Upon completion of the reaction, the mixture was allowed to cool naturally. The solids were then separated by centrifugation, washed with deionized water until neutral, and dried in a 100 °C oven. Finally, the material was calcined at 550 °C for 6 h in an air atmosphere to remove the template. The parent ZSM-5 molecular sieve is designated as NL-ZSM-5.

1.2 Preparation of mesoporous ZSM-5 zeolite

A 25% TPAOH aqueous solution purchased commercially was used as the stock solution, which was diluted to prepare 0.20, 0.30 and 0.40 mol/L TPAOH solutions. NL-ZSM-5 zeolites were added to the TPAOH solutions and placed in a stainless steel crystallization reactor lined with polytetrafluoroethylene. The mixture was heated to 170 °C for 8 h. After the reaction, the product was filtered and washed with deionized water until neutral. Subsequently, the product was then washed with 0.1 mol/L HCl at 80 °C for 1 h. The ion exchange was carried out with 1.0 mol/L NH₄NO₃ solution at 85 °C, repeated three times

for 2 h each. Finally, the resulting solid was calcined at 550 °C for 6 h. The three ZSM-5 variants subjected to different alkali treatments were designated ZSM-5-A, ZSM-5-B and ZSM-5-C, respectively.

1.3 Catalyst characterization

The crystal structure and phase composition of the catalyst were analyzed using a Bruker D8 ADVANCE X-ray diffractometer. Experimental conditions: Cu/K α radiation was used for scanning, with a wide-angle 2θ range of 5°–90°, a scanning speed of 5°/min, a scanning step size of 0.02°, an X-ray tube current of 40 mA and an X-ray tube voltage of 40 kV.

The Fourier transform infrared spectrometer (FT-IR) is performed by the TENSOR II model manufactured by BRUKER Corporation of Germany. The zeolite powder was uniformly mixed with potassium bromide (KBr) and pressed into pellets. The mass ratio of the two is 1 : 200.

The specific surface area and pore structure analyzer is the 3H-2000PMV series produced by Bestech Technology Co., Ltd. N₂ adsorption-desorption isotherms were measured at 77 K after degassing the samples at 200 °C for 6 h. The BET surface area S_{BET} was calculated from the Brunauer-Emmett-Teller equation in the relative pressure range $p/p_0 = 0.05\text{--}0.25$. The micropore surface area and volume (S_{micro} and v_{micro}) were obtained by the t -plot method. The total pore volume v_{total} was taken from the adsorbed N₂ volume at $p/p_0 \approx 0.99$. The pore size distribution was derived from the adsorption branch using an NL-DFT model.

The carbon deposition amount on the zeolite after the catalysis reaction was obtained by a thermogravimetric analyzer (TGA). The TA Q50 thermogravimetric analyzer (TGA) manufactured by Waters Corporation of the United States was adopted in this paper.

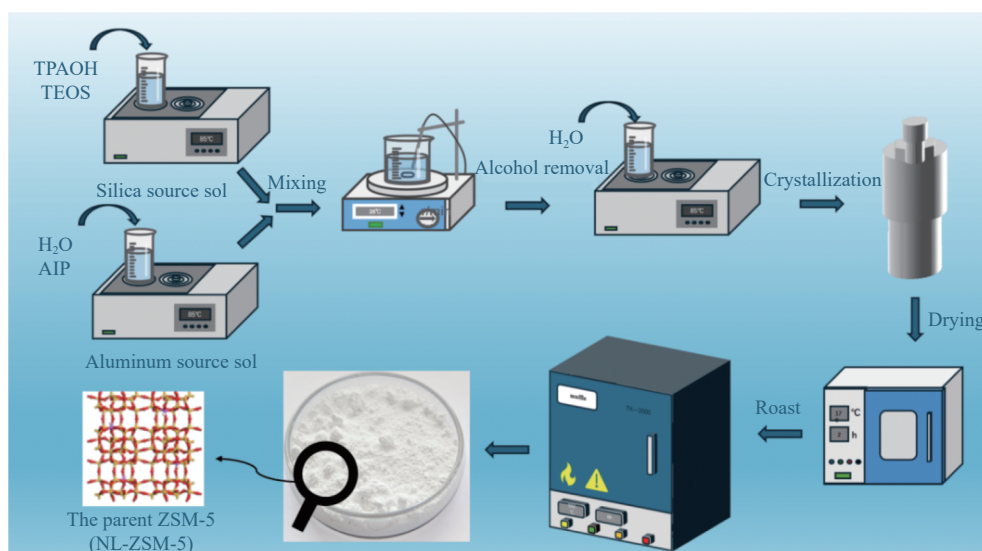


Fig. 1 The preparation process of the parent zeolite

During the test, a certain amount of sample was taken and subjected to a temperature-ramp test under an air atmosphere. The gas flow rate was 60 mL/min, and then the temperature was raised from room temperature to 900 °C at a heating rate of 10 °C/min.

The SiO₂/Al₂O₃ ratio of the zeolite was analyzed by an X-ray fluorescence spectrometer (XRF). The zeolite powder was uniformly mixed with boric acid and pressed into pellets.

The type of acid sites for the zeolite was characterized by pyridine Fourier transform infrared spectroscopy (Py-FTIR). Two sample groups were selected: a control group and a pyridine adsorption group. The control group was dried only at 80 °C. The pyridine adsorption group underwent pyridine adsorption under vacuum conditions for 24 h after drying, followed by desorption. Testing method: The control group served as the background. The pyridine adsorption group was scanned, and the Py-IR spectrum was obtained by comparing the two.

Scanning electron microscopy (SEM, ZEISS GeminiSEM 360 microscope) was used to obtain the morphology and microstructure of the samples. TEM images of the molecular sieves were acquired by a 200 kV field-emission transmission electron microscope (JEM-2100F) from Japan Electron Optics Laboratory. The electron beam was accelerated and focused by a 200 kV voltage before being projected onto the ultrathin sample. The crystal structure of the molecular sieves was then observed using optical microscopy. Prior to testing, the samples were dispersed in ethanol for 30 min.

1.4 Catalysis experiment

The benzene was selected and used as a model compound for coal tar. The catalytic reforming experiment was carried out in a fixed-bed reactor, as shown in Figure 2. The zeolite was ground to below 40 mesh and 2 g of it was placed in the isothermal zone of the fixed-bed reactor. Prior to the reaction, the interior of the reactor was purged with N₂ for 30 min to displace the internal air and remove moisture and other impurities adsorbed on the zeolite.

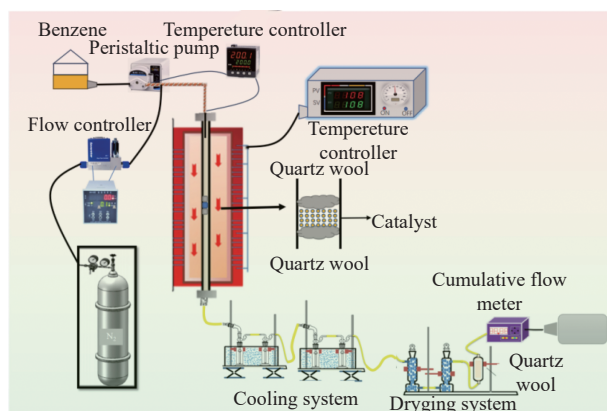


Fig. 2 The catalytic reforming experimental system

When the reaction temperature reaches the preset temperature, benzene is fed into the reactor at a feed rate of 1.0 mL/h. The outer surface of the connecting pipeline between the peristaltic pump and the reactor is wrapped with a heating tape to maintain benzene in a vaporized state. The total feeding time is 6 h. The feed flow rate was calibrated by the gravimetric method with the fluctuation controlled within $\pm 3\%$. The final reaction temperatures are set to 773, 823 and 873 K respectively.

1.5 Molecular simulation methods

Molecular modeling was employed to systematically investigate the adsorption-diffusion dynamics of benzene in hierarchical ZSM-5 at the molecular level and to elucidate the underlying structure-performance relationship linked to its coking propensity. All simulations were conducted on the Materials Studio 2023 commercial software platform.

This study primarily utilizes the Sorption and Forcite modules within the software. The Sorption module performs giant-regularized Monte Carlo (GCMC) simulations to calculate the adsorption isotherms and isothermal adsorption enthalpies of benzene molecules in ZSM-5 models with varying pore sizes, thereby evaluating their adsorption capacity and strength. The Forcite module runs molecular dynamics (MD) simulations. By analyzing the mean square displacement (MSD-T) of benzene molecules over time, it calculates their autodiffusion coefficient, thereby quantitatively evaluating the transport kinetics of molecules within the pores.

Through these simulations, we aim to theoretically derive microscopic parameters that are difficult to measure directly through experiments—such as adsorption heat, diffusion coefficients, and molecular spatial distribution—thereby elucidating at the molecular level the mechanism by which hierarchical porosity suppresses coke formation. This provides solid theoretical support and mechanistic explanation for the macroscopic phenomena observed experimentally, such as changes in TGA coke deposition and the evolution of BET pore structure.

2 Results and discussion

2.1 Physicochemical properties and structural characterization of zeolites

The XRD patterns of the NL-ZSM-5 and ZSM-5-A/B/C are presented in Figure 3, indicating that the characteristic peaks at 2θ values of 7.9°, 8.8°, 23.1°, 23.9° and 24.4° represent a typical MFI topological structure. This indicates that the crystal phase of the parent zeolite remains unchanged after TEOH treatment^[19]. As shown in Table 1, the relative crystallinity of hierarchical ZSM-5 zeolites decreases with increasing TEOH concentration.

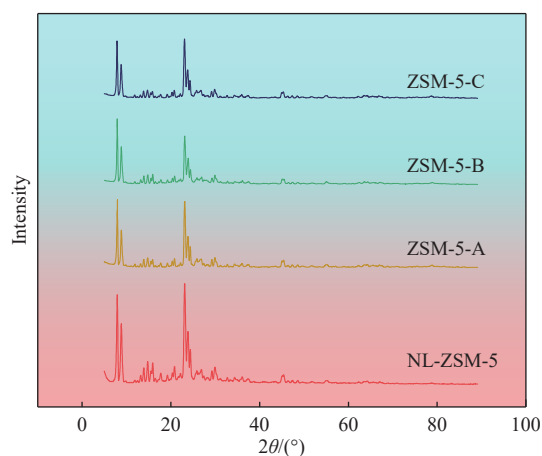
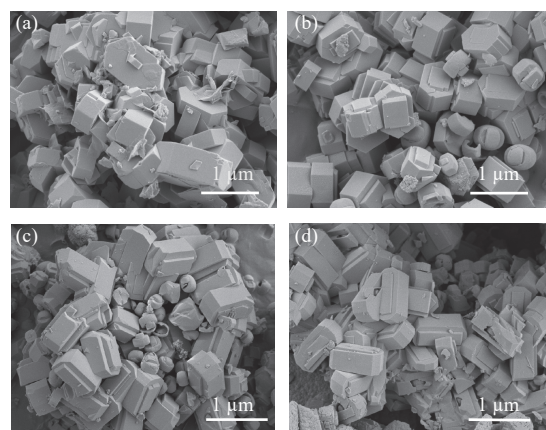


Fig. 3 The XRD patterns of the NL-ZSM-5 and ZSM-5-A/B/C



(a): NL-ZSM-5; (b): ZSM-5-A; (c): ZSM-5-B; (d): ZSM-5-C.

Fig. 4 The SEM images of different zeolites

Table 1 The crystallinity and Si/Al molar ratios of prepared ZSM-5 zeolites

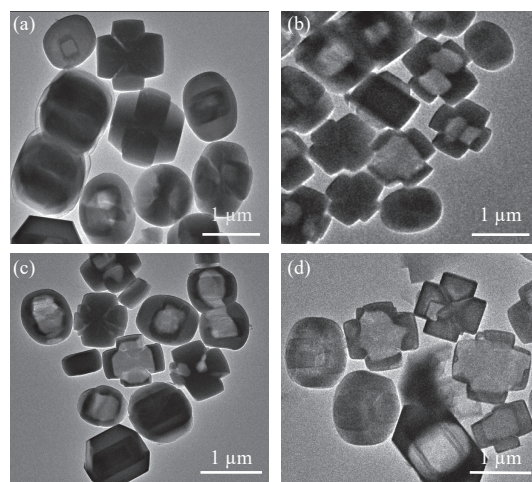
Sample	Relative crystallinity /%	SiO ₂ /Al ₂ O ₃ *
NL-ZSM-5	100	38.2
ZSM-5-A	99.4	37.6
ZSM-5-B	94.3	34.2
ZSM-5-C	89.7	30.9

*: Measured by XRF.

When the TEOAH concentration increases from 0 to 0.4 mol/L, the Si/Al molar ratio decreases from 38.2 to 30.9, indicating that desilication is the dominant process during the treatment. In an alkaline medium, the hydrolysis/dissolution rate of Si–O–Si bonds is generally higher than that of Si–O–Al bonds. Moreover, the negative charge of framework AlO_4^- and the coordination “protection” of organic ammonium cations (TEA^+) inhibit the corrosion of the near aluminum sites, resulting in a continuous decrease in the silica-alumina ratio and relative crystallinity of ZSM-5^[20].

The SEM and TEM images of NL-ZSM-5 and ZSM-5-A/B/C (Figure 4 and Figure 5) indicate that the crystal morphology and outline of the parent ZSM-5 are basically well-preserved. As the TEOAH concentration increases, the outer shells of some crystals in the treated ZSM-5-A/B/C zeolites undergo varying degrees of damage. In addition, as shown in Figure 5, as the TEOAH concentration increases, hollow zone appears inside the zeolites, exhibiting the characteristics of shell-core cavitation and shell layer rearrangement.

The N₂ adsorption-desorption isotherms and pore size distributions of different zeolites are presented in Figure 6. The adsorption behavior of ZSM-5-A/B/C in the low pressure region is similar to that of the NL-ZSM-5 zeolite. In the high pressure region, ZSM-5-A/B/C exhibit typical H4-type hysteresis loops in their adsorption isotherms. As the TEOAH concentration increases, the hysteresis loops expand, indicating that the increase in TEOAH concentration leads to a continuous rise in the mesopore volume of the zeolites.

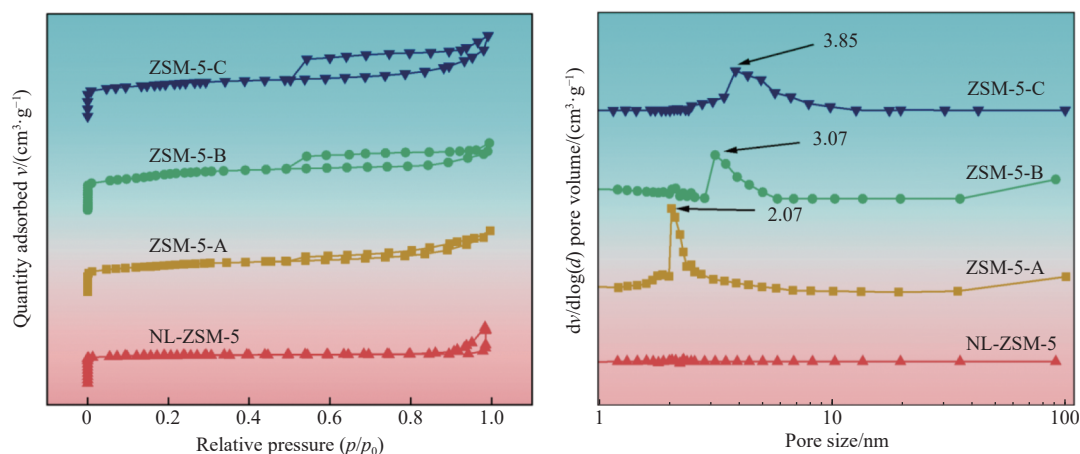


(a): NL-ZSM-5; (b): ZSM-5-A; (c): ZSM-5-B; (d): ZSM-5-C.

Fig. 5 The TEM images of different zeolites

As shown in Figure 6(b), the pore size distributions as determined by NL-DFT reveal the formation of mesopores with diameters in the range of 2–4 nm within the ZSM-5-A/B/C samples. The most probable pore sizes of ZSM-5-A/B/C are 2.07, 3.07 and 3.85 nm, respectively, which further confirms that the most probable pore size and mesopore volume increase continuously. The specific surface areas and total pore volumes of NL-ZSM-5 and ZSM-5-A/B/C are presented in Table 2. As the TEOAH concentration increases, the total pore volumes of ZSM-5-A/B/C increase, while their specific surface areas and micropore volumes decrease.

The FT-IR spectra of different zeolites are presented in Figure 7, indicating that the characteristic bands of the MFI framework near 1098, 800, 550 and 450 cm^{−1} remain distinct. This indicates that the overall framework integrity of ZSM-5 is maintained. The variation in the T–O–T asymmetric stretching peak near 1230 cm^{−1} is consistent with the decrease in the Si/Al molar ratio (caused by the relative enrichment of Al due to selective desilication) determined by XRF, reflecting changes in the local chemical environment of the framework.

Fig. 6 The N₂ adsorption-desorption isotherms and pore size distributions of NL-ZSM-5 and ZSM-5-A/B/CTable 2 Textural properties of NL-ZSM-5 and TEOAH-treated ZSM-5 zeolites derived from N₂ adsorption at 77 K

Sample	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$S_{\text{ext}}/(\text{m}^2 \cdot \text{g}^{-1})$	$v_{\text{total}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$v_{\text{micro}}/(\text{cm}^3 \cdot \text{g}^{-1})$
NL-ZSM-5	433	41	0.24	0.11
ZSM-5-A	336	38	0.32	0.09
ZSM-5-B	326	36	0.35	0.08
ZSM-5-C	318	28	0.43	0.05

* S_{BET} is the BET surface area ($p/p_0 = 0.05-0.25$). S_{micro} and v_{micro} are from the t -plot method. v_{total} is the adsorbed volume at $p/p_0 \approx 0.99$.

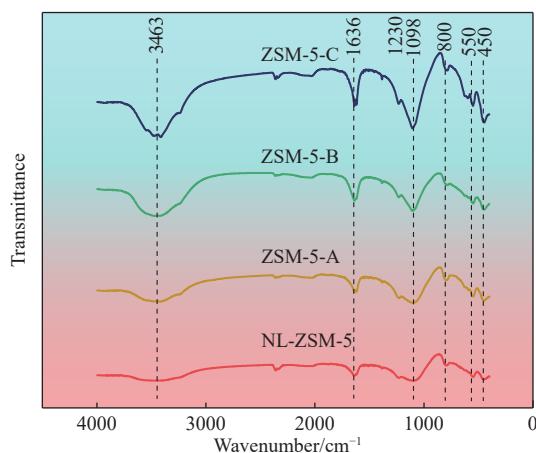


Fig. 7 The FT-IR spectra of NL-ZSM-5 and ZSM-5-A/B/C

In addition, as the TEOAH concentration increases, the intensities of the peaks at 3463 cm^{-1} (O–H stretching vibration) and 1636 cm^{-1} (H–O–H bending vibration) gradually increase. The formation of mesopores creates new surfaces, and the dangling bonds on these surfaces react with water to *in situ* generate silanol groups (Si–OH), thereby leading to the enhancement of the –OH signal in FT-IR. It is precisely the increase in the number of mesopores that leads to the enhancement of the –OH peak, which is also consistent with the result of the continuous increase in mesopore volume from the BET analysis.

In addition, SEM/TEM images show that the overall crystal outline is retained, with minimal particle fragmentation. The external specific surface area (S_{ext}) decreases slightly, which indicates that mesopores are mainly formed inside the crystals. In conclusion, the post-

treatment with TEOAH retains the MFI framework. Internal desilication introduces mesopores while simultaneously increasing surface silanol groups and defect sites. This modification provides a structural basis for enhancing molecular mass transfer and regulating the accessibility of acidic sites.

The pyridine Fourier transform infrared (FT-IR) spectra of NL-ZSM-5 and ZSM-5-A/B/C are presented in Figure 8. The characteristic bands near 1545 and 1648 cm^{-1} correspond to pyridinium ions (PyH^+) formed by pyridine adsorbed on Brønsted acid sites. The characteristic bands near 1450 and 1610 cm^{-1} are attributed to pyridine coordinated with Lewis acid sites. The band near 1490 cm^{-1} is a mixed band contributed by both Brønsted (B) and Lewis (L) acid sites. As the TEOAH concentration increases, the intensities of the aforementioned bands showed an overall increasing trend. In ZSM-5, Brønsted acid sites arise from framework aluminum in bridged Si–OH–Al groups, while Lewis acid sites are primarily associated with extra-framework aluminum species and partially coordinated aluminum centers. The combined treatment of Al-protected TEOAH desilication and HCl washing raises the total acid site concentration. This is achieved not only by exposing more framework Al to generate additional Brønsted acidity (after proton exchange) but also by producing extra-framework Al that contributes to Lewis acidity^[21]. Meanwhile, the formation of intracrystalline mesopores and hollow structures markedly improves the accessibility of internal Brønsted sites that were previously located in strongly confined micropores, so that the accessible Brønsted acidity increases more strongly than the accessible Lewis acidity^[22].

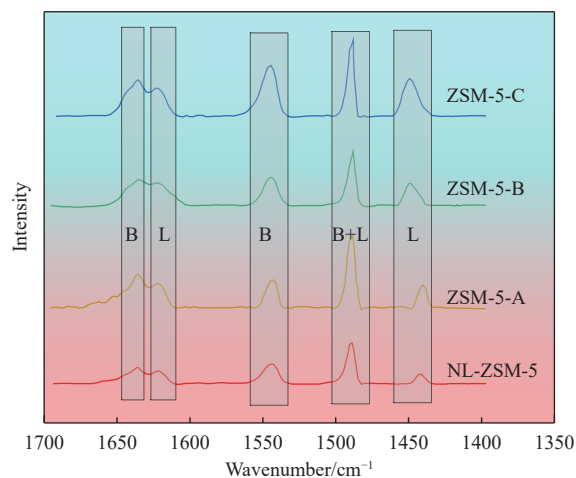


Fig. 8 The pyridine Fourier transform infrared spectra of NL-ZSM-5 and ZSM-5-A/B/C

As a result, both Brønsted and Lewis acid amounts are higher than in NL-ZSM-5, but the Brønsted fraction becomes dominant and the measured L/B ratio gradually

decreases from ZSM-5-A to ZSM-5-C, as shown in Table 3.

2.2 Effect of temperature and pore structure on the coking behavior of ZSM-5

2.2.1 Effect of pore structure on the coking behavior of ZSM-5

The analysis of coking amounts for NL-ZSM-5 and ZSM-5-A/B/C during the catalytic reforming of benzene is presented in Figure 9, indicating that the parent zeolite NL-ZSM-5 exhibits the highest coking amount of 11.2%. As the TEAOH concentration and mesopore content increase, the coke amounts of ZSM-5-A/B/C decrease continuously. When the pore diameter reaches around 3.85 nm, the coke amount of ZSM-5-C zeolite during the catalytic reforming of benzene is 4.0%, which is only one-third of that of the parent sample. This is due to the fact that intermediates such as benzene and its derivatives tend to be trapped in the microporous channels, leading to coke formation^[23].

Table 3 Acidic properties of NL-ZSM-5 and ZSM-5-A/B/C

Zeolite	Acid amount/(mmol·g ⁻¹)			L/B
	total	B	L	
NL-ZSM-5	0.72	0.28	0.44	1.57
ZSM-5-A	0.95	0.42	0.53	1.26
ZSM-5-B	1.07	0.50	0.57	1.14
ZSM-5-C	1.28	0.67	0.61	0.91

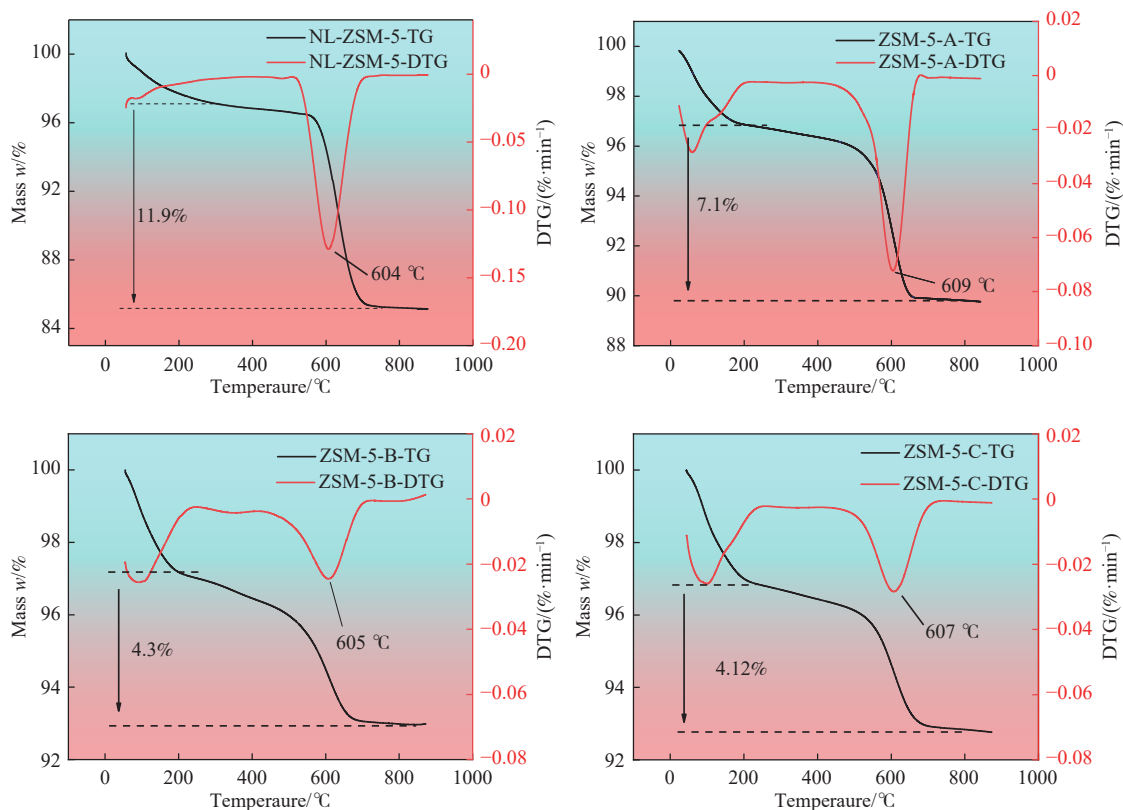


Fig. 9 The TG/DTG curves of the prepared matrix and the ZSM-5 molecular sieve treated with TEAOH

However, the formation of mesoporous channels improves the diffusion of product molecules, thereby effectively reducing the coking rate. In addition, a main peak appears at approximately 600 °C in the DTG curve, indicating that the deposited coke is dominated by hard coke, which is difficult to be oxidized^[24]. In addition, the combined BET and Py-IR results further clarify the influence of acidity on the coking behaviour. TEOH treatment introduces intracrystalline mesopores and hollow structures by selective desilication, which decreases the micropore fraction, and exposes more framework aluminium at the same time, leading to higher amounts of both Brønsted and Lewis acid sites, as shown in Figure 8 and Table 3. The BET and NL-DFT analyses reveal an almost linear positive correlation between the micropore fraction and the coke amount (Figure 12), indicating that the coking tendency is mainly governed by the enrichment of strong acid sites^[25–27]. In the unmodified NL-ZSM-5, many acid sites are concentrated inside narrow micropores, where aromatic intermediates experience long residence times and high local concentrations and readily undergo multi step condensation to form coke that blocks the micropores. After TEOOH modification, part of the acid sites are exposed to mesoporous and external surfaces, and the newly formed mesopores provide more open diffusion pathways, allowing intermediates and products to leave the confined regions before deep condensation occurs, so that micropore blocking coke is effectively suppressed even though the total acidity is increased.

The XRD patterns of different zeolites after catalytic reaction are illustrated in Figure 10. The MFI characteristic diffraction peak at $2\theta \approx 23^\circ$ reveals notable differences among the post-reaction samples. The diffraction peak of the NL-ZSM-5 sample, which exhibits higher carbon accumulation, shifts slightly toward lower angles. In contrast, the peaks of the TEOOH-treated samples (ZSM-5-A/B/C) progressively stabilize and shift closed to the positions observed for the parent ZSM-5. This observation suggests that carbon accumulation within the pores exerts lattice stress on the ZSM-5 crystal structure, resulting in

peak displacement^[28–29]. With increasing concentrations of TEOOH treatment, the introduction of a mesoporous structure effectively reduces carbon accumulation within the micropores. This reduction mitigates interference with the crystal structure and preserves higher structural integrity. These results are consistent with the coking trends observed in the TG/DTG analysis, thus providing further evidence that TEOOH modification effectively suppresses coke deposition and helps preserve the crystalline structure.

The BET curves of different ZSM-5 zeolites after catalytic reforming reaction are listed in Figure 11, indicating that all samples exhibit a common trend. The accessible pore structure undergoes attenuation while the hierarchical characteristics remain intact. As indicated in Table 4, after the reaction, the specific surface areas of ZSM-5-NL/A/B/C decreased from 433/336/326/318 to 378/298/277/223 m²/g, respectively. The total pore volumes exhibited only minor reductions (0.24→0.20, 0.32→0.25, 0.35→0.29, 0.43→0.36 cm³/g), suggesting that the accessible pore volume of the hierarchical pores treated with TEOOH remained substantial after the reaction. For instance, ZSM-5-C retained 36 cm³/g, which is significantly higher than that of ZSM-5-NL 20 cm³/g. The most notable changes were observed in micropore volume: NL/A/B/C decreased from 0.11/0.09/0.08/0.05 to 0.05/0.04/0.03/0.02 cm³/g. The reduction quantity reaches approximately 55%, 56%, 62% and 60%, respectively. As a result, the proportion of micropores in the total pore volume after the reaction was significantly reduced from 46%, 28%, 23% and 12% to 25%, 16%, 10% and 5.6%. In contrast, the external surface area exhibited only a slight decrease (NL: 41→29, A: 38→27, B: 36→26, C: 28→22 m²/g), highlighting the more substantial reduction in specific surface area. These observations suggest that micropore accessibility was the primarily and most significantly compromised during the reaction, as it was partially obscured by deposits and accompanied by localized “coarsening”. In contrast, mesoporous channels exhibited greater resilience, continuing to serve as effective pathways for molecular diffusion after the reaction.

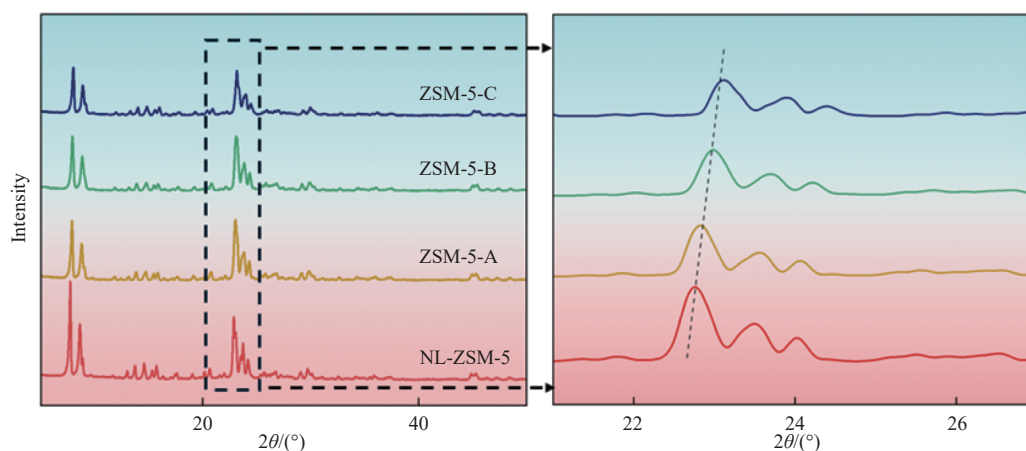


Fig. 10 The XRD of different zeolites after catalytic reaction

A significant correlation between the microporous fraction and coking behavior is evident, as illustrated in Figure 12. The coke deposition amount decreases continuously with the reduction of the micropore proportion in the zeolites, showing a significant near-linear correlation. It is important to note that the kinetic diameter of benzene is approximately 0.59 nm. It matches with the 10-membered ring pores of ZSM-5 (0.53–0.56 nm), resulting in restricted diffusion and prolonged residence time of the species within the micropores. Following alkylation, the volume of benzene further increases, rendering it more susceptible to sequential condensation and retention within the micropores. Consequently, the micropore-dominated structure is more prone to the formation of coke deposits within the pores. The introduction of mesopores through

TEAOH treatment creates additional diffusion pathways, thereby mitigating the coking rate associated with this critical size matching. This explains why unmodified NL-ZSM-5 exhibits the highest level of coke formation during benzene conversion.

2.2.2 Effect of reaction temperature variations on carbon characteristics

The XRD patterns of ZSM-5 zeolites after catalytic reactions at different temperatures are showed in Figure 13, indicating that there are significant differences in the characteristic MFI diffraction peaks of the post-reaction samples at $2\theta \approx 23^\circ$.

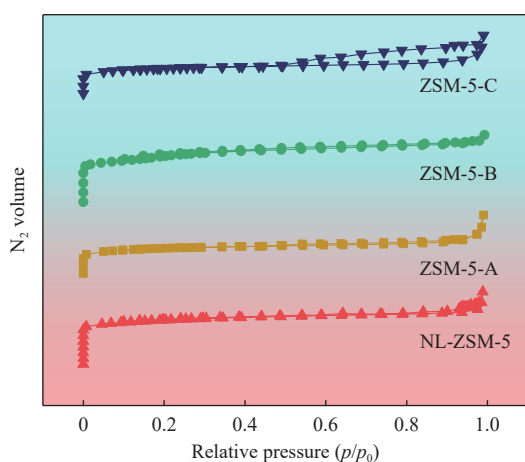


Fig. 11 The BET curves of different ZSM-5 zeolites after catalytic reforming reaction

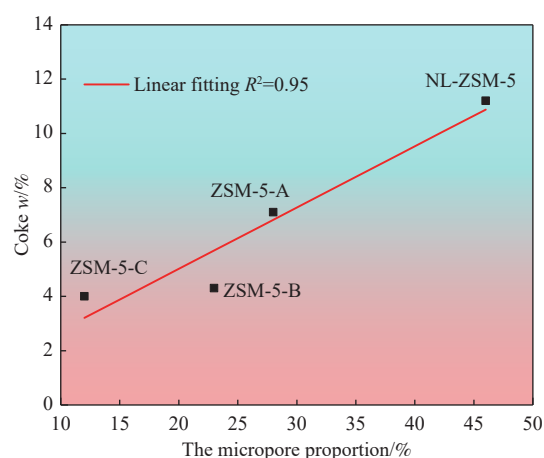


Fig. 12 Linear fitting between the micropore proportion and the coke deposition amount

Table 4 Textural properties of spent NL-ZSM-5 and TEOAH-treated ZSM-5 catalysts derived from N_2 adsorption at 77 K

Sample	$S_{BET}/(m^2 \cdot g^{-1})$	$S_{ext}/(m^2 \cdot g^{-1})$	$v_{total}/(cm^3 \cdot g^{-1})$	$v_{micro}/(cm^3 \cdot g^{-1})$
NL-ZSM-5	378	29	0.20	0.05
ZSM-5-A	298	27	0.25	0.04
ZSM-5-B	277	26	0.29	0.03
ZSM-5-C	223	22	0.36	0.02

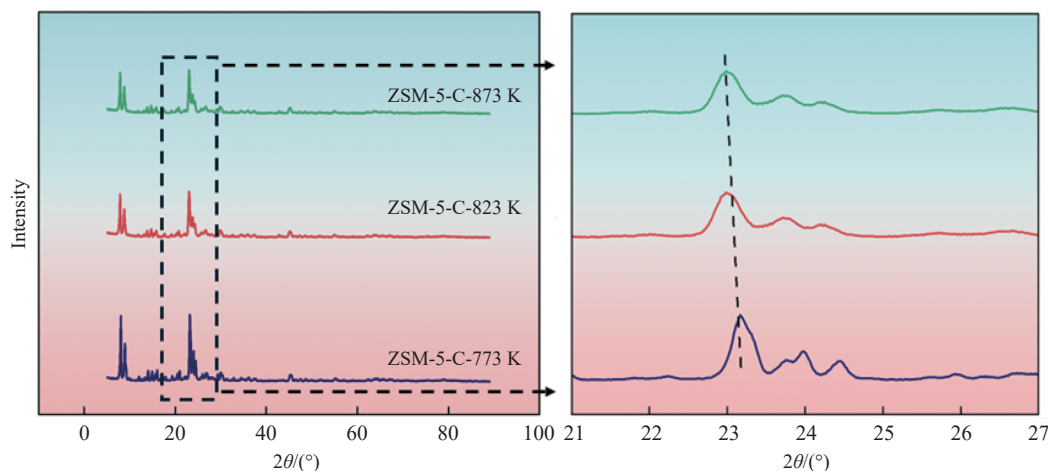


Fig. 13 The XRD patterns of ZSM-5 zeolites after catalytic reactions at different temperatures

The NL-ZSM-5 sample, which exhibits higher carbon deposition, demonstrates a slight shift of the diffraction peak toward lower angles. In contrast, as the coke content diminished in the TEOAH-treated samples (ZSM-5-A/B/C), their peak positions progressively stabilized and were restored to near those of the parent ZSM-5. This observation suggests that carbon accumulation within the pores induces lattice stress on the ZSM-5 crystal structure, resulting in peak displacement. As the concentration of TEOAH treatment increases, the introduction of a mesoporous structure effectively reduces carbon accumulation within the micropores. This reduction mitigates interference with the crystal structure, thereby preserving greater structural integrity. These findings are consistent with the trend of coke amounts observed in TG/DTG analysis, further corroborating the beneficial role of TEOAH modification in suppressing carbon buildup and safeguarding the crystal structure.

The adsorption isotherms of ZSM-5-C zeolite at various catalytic temperatures are listed in Figure 14. The N_2 adsorption capacity demonstrates notable variations with relative pressure (p/p_0), indicating the sensitivity of the zeolite pore structure to the catalytic reaction temperature. Further analysis of the pore structure parameters in Table 5 indicates that as the catalytic reaction temperature rises from 773 to 873 K, the specific surface area (S_{BET}) of the sample decreases from 265 to 177 m^2/g , the total pore volume (v_{total}) declines from 0.44 to 0.25 cm^3/g , and the micropore volume (v_{micro}) diminishes from 0.03 to 0.01 cm^3/g . This trend suggests that increasing the catalytic reaction temperature significantly accelerates the kinetic rate of the reaction system, which is manifested as more vigorous molecular motion and improved compatibility of intermolecular interactions. However, the desorption and escape of reaction intermediates or product molecules become more difficult, which directly enhances the tendency of benzene molecules and their derivatives to polymerize and form carbon deposits within the zeolite channels^[30–31].

Existing studies have elucidated the relationship between elevated temperatures and coking behavior in ZSM-5 zeolites from various perspectives. On one hand, the high-temperature environment facilitates the decomposition of carbon deposits, theoretically reducing coke blockage within the channels^[32–34]. On the other hand, the kinetic rate of catalytic reactions accelerates significantly at higher temperatures. This increase intensifies molecular motion and enhances the compatibility of intermolecular interactions, thereby complicating the desorption and escape of reaction intermediates or product molecules. As a result,

the rate of coking formation within the pores escalates, exceeds the rate of coke decomposition. The detrimental effects of coke covering active sites and obstructing micropores remain predominant. Furthermore, studies indicate that when the catalytic reaction temperature of ZSM-5 zeolites exceeds 873 K, it approaches the threshold for irreversible damage to the pore framework, particularly concerning the loss of micropores. The simultaneous occurrence of pore collapse and particle sintering during the reaction directly undermines the integrity of both micropores and mesopores. This structural damage, distinct from carbon deposition effects, further exacerbates the deterioration of the pore structure^[35–36].

In summary, the porosity and specific surface area of the sample reached their minimum values following the catalytic reaction at 873 K. While elevated temperatures facilitate the decomposition of carbon deposits, this beneficial effect is insufficient to counteract the dual negative consequences of rapid carbon deposit formation and damage to the pore network framework, ultimately resulting in substantial deterioration of the pore structure. Consequently, it is crucial to balance reaction temperature and catalyst stability to avert excessive temperatures that could compromise the integrity of the catalyst structure.

The TG/DTG analysis of different reaction temperatures for ZSM-5-C are listed Figure 15, indicating that the reaction temperature significantly influenced the coke accumulation amount of the catalyst. As the reaction temperature increased from 773 to 873 K, the molecular sieve coking amount showed an increasing trend. From the perspective of thermodynamics, increasing the temperature shifts the equilibrium of the system toward the dehydrogenation-aromatization direction with a lower H/C ratio.

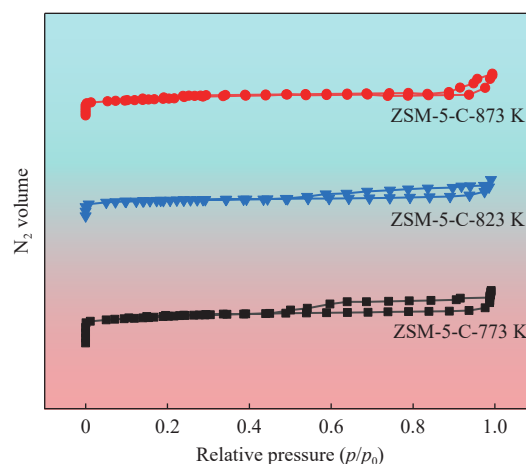


Fig. 14 The BET adsorption isotherms of ZSM-5-C at various catalytic temperatures

Table 5 Textural properties of spent ZSM-5-C catalysts derived from N_2 adsorption at 77 K after reaction at different temperatures

Sample	$S_{BET}/(m^2 \cdot g^{-1})$	$S_{ext}/(m^2 \cdot g^{-1})$	$v_{total}/(cm^3 \cdot g^{-1})$	$v_{micro}/(cm^3 \cdot g^{-1})$
ZSM-5-C-873 K	177	17	0.25	0.01
ZSM-5-C-823 K	223	22	0.36	0.02
ZSM-5-C-773 K	265	28	0.44	0.03

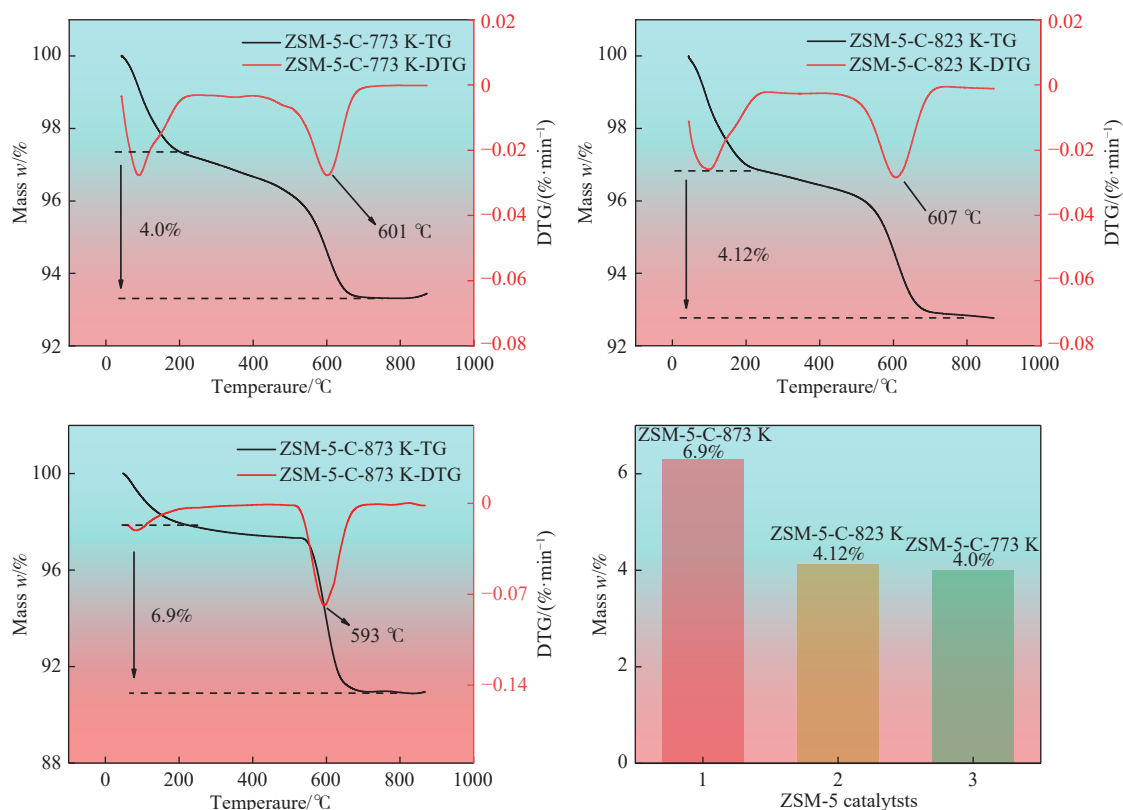


Fig. 15 The TG/DTG analysis of different reaction temperatures for ZSM-5-C

The micropore confinement provides additional stabilization to these more conjugated species, resulting in a stronger driving force for their formation^[37]. From a kinetic perspective, relevant steps such as oligomerization, cyclization, and hydrogen transfer exhibit pronounced temperature dependence. Elevated temperatures accelerate formation rates. However, once larger, less polar heavy aromatic intermediates form, their desorption and diffusion within ZSM-5 channels become less favorable^[38]. This leads to longer effective residence times and slower diffusion, which is manifested as enhanced coke growth under high-temperature conditions.

2.3 Molecular simulation studies

Although the calculated values for the most probable pore diameters were 2.07, 3.11 and 3.85 nm, this study adopted regularly spaced pore diameters (2.0, 2.5 and 3.0 nm) in the simulations in favor of the precisely determined experimental values. This methodology serves two primary purposes. First, the simplified pore size parameters offer a clearer depiction of the overall performance as pore size varies, thereby facilitating comparative analysis among different data points. Second, the pore size values are organized in increments of 0.5 nm, resulting in a more uniform distribution of data points. This uniformity aids in developing a more systematic data model and in plotting clear result curves, which enables standardized analysis of the simulation outcomes. Additionally, the minimal parameter changes between adjacent simulation

conditions limit the necessary model adjustments for each calculation, thereby reducing computational overhead and significantly improving simulation efficiency. Finally, the deviations between these selected apertures and the actual calculated values remain within acceptable limits, ensuring the reliability of the overall research conclusions.

2.3.1 Model construction and validation

Crystallographic analysis of the ZSM-5 unit cell model was performed using the Reflex module within the Materials Studio 2023 software package. As illustrated in Figure 16, the simulated XRD patterns displayed characteristic diffraction peaks at $2\theta = 7.9^\circ, 8.8^\circ, 23.1^\circ, 23.8^\circ$ and 24.4° , which are in full agreement with those of the standard MFI topology. These findings confirm that the constructed model aligns closely with the crystal structure of the experimentally synthesized sample, thereby providing preliminary validation of the structural integrity of the fundamental model.

To further validate the reliability of the hierarchical model in describing actual adsorption behavior, CO_2 was employed as a probe molecule. Its adsorption isotherm in a hierarchical ZSM-5 model with a pore size of approximately 3 nm was simulated at 273 K. The simulated results were compared with experimental data reported by Liu and their team^[39]. As illustrated in Figure 17, the simulated adsorption amounts demonstrate a high degree of agreement with the experimental data, effectively reproducing the adsorption trend of CO_2 on actual molecular sieve materials.

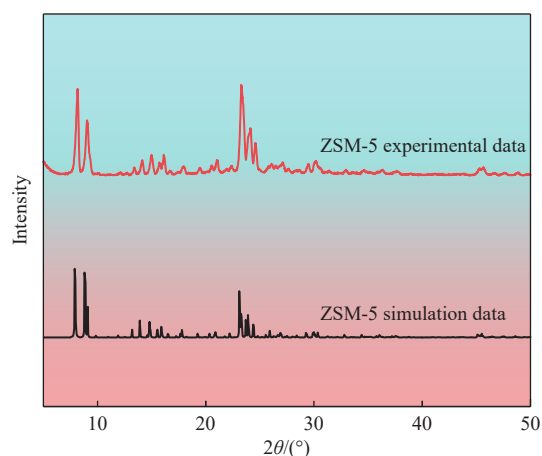


Fig. 16 Comparison between experimental and simulated XRD values of ZSM-5 zeolites

Although the simulated values are slightly higher than the experimental values, this discrepancy can be primarily attributed to the ideal crystal model, which features a perfectly defect-free pore structure and enhanced porosity, thereby circumventing issues such as grain boundaries, pore blockage, or partial collapse that are present in actual materials. This comparison affirms the reliability of the constructed multi-pore model regarding its adsorption performance.

Detailed model construction steps, force field parameters, simulation ensembles, and calculation procedures are provided in the Supporting Information. In summary, the above analyses confirms the structural accuracy and performance reliability of the simulation model employed in subsequent studies of benzene molecule adsorption and diffusion behavior, thereby establishing a foundation for the credibility of the entire simulation research.

2.3.2 Adsorption behavior and heat of adsorption

To assess the adsorption performance of benzen in hierarchical ZSM-5 molecular sieves, the adsorption isotherms and corresponding adsorption enthalpies were calculated under varying pore sizes at temperatures of 773,

823 and 873 K. As illustrated in Figure 18, the equilibrium adsorption amount of benzene exhibits an inverse relationship with the mesopore size at a constant temperature. This trend is in full agreement with experimental BET measurements, which show a decrease in micropore volume with increasing TEOAH treatment intensity. This suggests that the micropores serve as the main sites responsible for benzene adsorption. The partial destruction of the micropore structure during mesopore formation directly reduces the effective micropore volume available for benzene adsorption and diminishes high-energy adsorption sites, resulting in an overall decrease in adsorption capacity. At constant pressure, the equilibrium adsorption capacity of benzene significantly declines with rising temperature. This phenomenon occurs because benzene adsorption on ZSM-5 is an exothermic physical adsorption process, and higher temperatures impede the adsorption process. At elevated temperatures, benzene molecules gain sufficient kinetic energy to desorb more readily from adsorption sites, hence a decline in their equilibrium adsorption capacity in the pores. This trend is consistent with fundamental thermodynamic principles that govern adsorption processes.

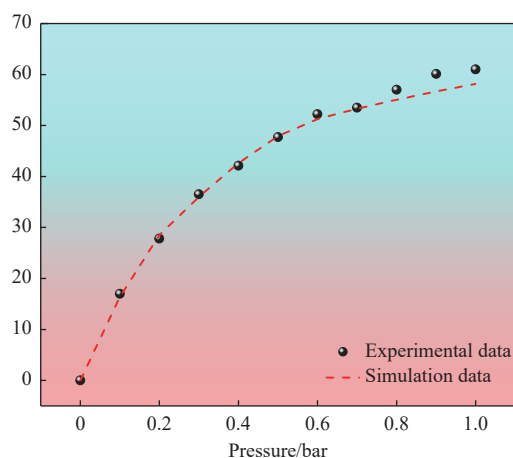


Fig. 17 Comparison between simulated and experimental CO_2 adsorption isotherms of hierarchical ZSM-5 zeolites

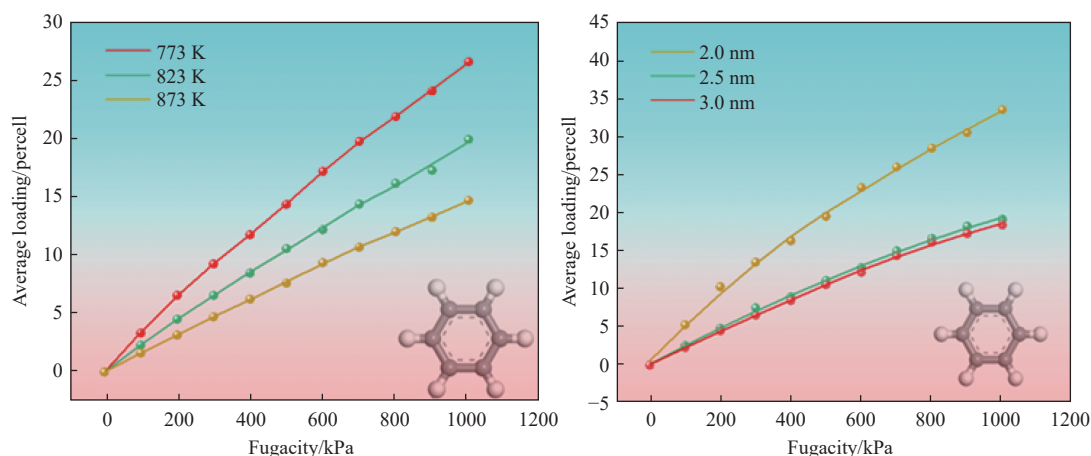


Fig. 18 Adsorption isotherms of benzene on ZSM-5 zeolites with different pore sizes and temperatures

The adsorption heat curves of benzene at various temperatures on ZSM-5 molecular sieves with differing pore sizes are shown in Figure 19, indicating that the adsorption heat exhibits a consistent decrease with increasing temperature in the 3.0 nm mesoporous model. This phenomenon can be attributed to the heterogeneous energy distribution of adsorption sites on the solid surface. At lower temperatures, molecules can occupy multiple sites, including a significant number of weakly bound locations, leading to an overall average measurement of adsorption heat. As the temperature increases, molecules preferentially desorb from these weakly bound sites, ultimately leaving only those bound to the highest-energy sites. Consequently, the reduced adsorption heat observed at elevated temperatures does not imply a universal weakening of all interactions, but rather indicates that the population of occupied adsorption sites becomes concentrated toward those with higher energies. Nonetheless, even at these high-energy sites, vigorous molecular thermal motion results in an apparent binding energy that is lower than its value at lower temperatures. Furthermore, at a constant temperature, the adsorption heat value exhibits a slight decrease with

increasing pore size. This trend indicates that in the minimal-pore ZSM-5 model (2.0 nm), benzene molecules experience the most pronounced spatial confinement effects, thereby their van der Waals interactions with the pore walls are maximized. The introduction of mesopores generates diffusion pathways while simultaneously diluting this highly confined environment, resulting in benzene molecules being, on average, situated within an adsorption environment characterized by relatively weaker interactions^[40].

2.3.3 Adsorption density distribution

The adsorption density distribution of benzene on ZSM-5 zeolites across various pore sizes and temperatures are listed in Figure 20. A comparison of the density distributions for the same pore size model at different temperatures (773–873 K) reveals a distinct trend. An increase in temperature leads to decrease in adsorption density distribution. At 773 K, benzene molecules form localized region of high-density within confined spaces, such as pore intersections, of the 3.0 nm mesopore model.

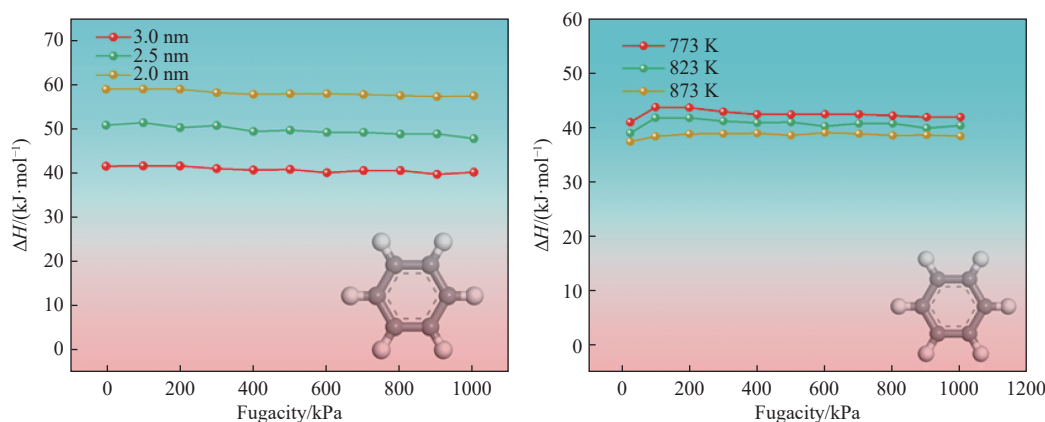


Fig. 19 Adsorption heat curves of benzene on ZSM-5 zeolites with different pore sizes and temperatures

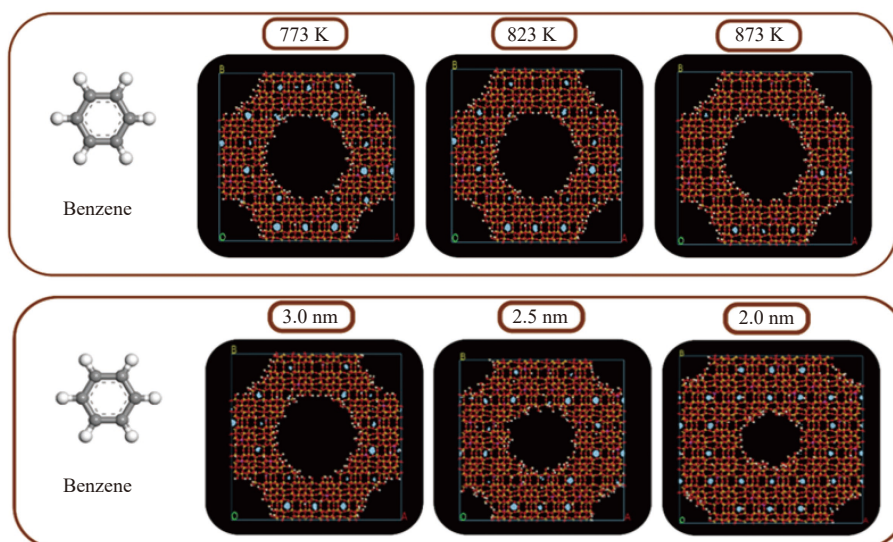


Fig. 20 Adsorption density distributions of benzene on ZSM-5 zeolites under different pore sizes and temperatures

As the temperature rises to 873 K, enhanced molecular thermal motion increases the kinetic energy of the molecules, enabling them to readily escape from the strongest adsorption sites. This observation is consistent with the finding in Section 2.3.2 that adsorption heat diminishes with rising temperature, thereby indirectly demonstrating that elevated temperatures reduce the average interaction forces between benzene molecules and the pore channels.

As the mesopore diameter increases from 2.0 to 3.0 nm, the spatial distribution characteristics of benzene molecules within the pore channels exhibit significant alterations. In ZSM-5 with a mesopore diameter of 2.0 nm, benzene molecules display a marked spatial aggregation effect. Density contour plots indicate a high concentration of benzene at pore junction regions (~ 0.55 nm) and the sinuous bends of the sinusoidal channels. This nanoscale spatial confinement effect results in notably elevated local concentrations, creating adsorption “hotspot” regions. Furthermore, GCMC simulations suggest that the majority of benzene adsorption occurs in micropores, thereby demonstrating that micropores retain their primary role in adsorption.

2.3.4 Molecular diffusion kinetics

The MSD-T curves of benzene in ZSM-5 for different pore sizes and temperatures are presented in Figure 21, indicating that the diffusion of benzene molecules is jointly influenced by temperature and pore size. When the temperature is raised from 773 to 873 K in the 3.0 nm pore model, the diffusion coefficient increases from 6.95×10^{-5} to 2.77×10^{-4} cm²/s, representing a fourfold increase. This trend is in accordance with the principle that higher temperatures provide molecules with greater kinetic energy, thereby enhancing their migratory capacity. Conversely, at a constant temperature of 823 K, a reduction in pore size from 3.0 to 2.0 nm leads to a significant decrease in the diffusion coefficient from 1.48×10^{-4} to 3.74×10^{-5} cm²/s, corresponding a 75% reduction. This phenomenon suggests that although temperatures facilitated diffusion, the influence of pore sizes reduction on hindering on mass

transfer is even more pronounced. A smaller pore size not only intensifies interactions between molecules and pore wall surfaces but also increases the complexity of diffusion pathways, collectively slowing their overall transport through the channel system. The synergistic effects of temperature and pore size indicate that pore dimensions exert a more significant constraint on diffusion behavior under high-temperature reaction conditions. This finding reveals the intricate nature of mass transfer in hierarchical ZSM-5 catalysts and provides essential insights into coking mechanisms. Although high temperatures enhance molecular diffusion capacity, narrower pore structures considerably prolong the molecular residence time within the channels, thereby establishing the probability of deep reactions and coke formation. These results underscore that catalyst design must carefully balance the synergistic interplay between temperature and pore size, which requires the strategic optimization of pore architecture to achieve an optimal trade-off between reaction efficiency and coking resistance.

2.3.5 Mechanism elucidation

By combining macroscopic and microscopic analyses, this work deciphers the synergistic effects of reaction temperature and pore structure on coke formation during benzene conversion over ZSM-5 catalysts. In previous research, the reduction in carbon deposition has predominantly been attributed to enhanced diffusion resulting from the introduction of mesopores. However, simulations and BET data from this study indicate that a reduction in adsorption sites is equally critical. First, the rise in mesoporosity results in a systematic decrease in both the adsorption amount and adsorption heat of benzene. This indicates that TEAOH treatment, in creating mesopores, partially damages the micropore structure which hosts high-energy adsorption sites—an effect often considered a structural “sacrifice”. Nevertheless, this “sacrifice” yields significant kinetic advantages. the diffusion coefficient of benzene molecules in larger pores (e.g., 3.0 nm) increases nearly fourfold compared to that in confined environments (e.g., 2.0 nm) (1.48×10^{-4} vs. 3.74×10^{-5}).

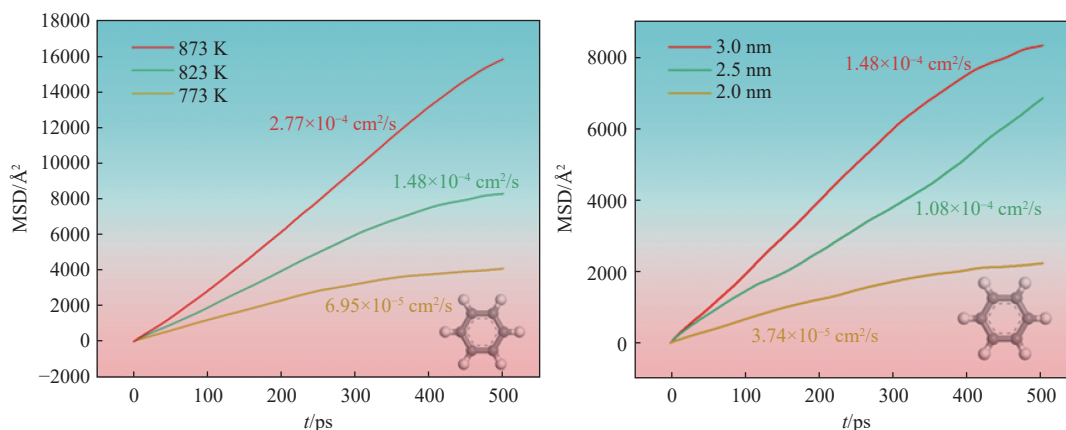


Fig. 21 MSD-T curves and diffusion coefficients of benzene in ZSM-5 zeolites under different pore sizes and temperatures

Therefore, this study posits that the anti-coking advantage of mesopores arises from a moderate sacrifice of strong adsorption capacity for reactant molecules, which is compensated by a substantial enhancement of their diffusivity. The anti-coking mechanism encompasses two aspects. 1—Diffusion enhancement mechanism: Mesopores serve as a “highway” for molecular transport, significantly reducing the residence time of benzene molecules and their derivatives within the pore channels, thereby allowing them to diffuse away before undergoing deeper reactions. 2—Adsorption site regulation mechanism: Although the etching of some micropores does not reduce the total number of strong acid sites—indeed, Py-IR data show the total Brønsted acidity increases from 0.28 to 0.67 mmol/g upon modification—it does reduce the proportion of those strong sites located within highly confined micropore environments that are prone to initiating deep condensation. At the same time, the L/B ratio decreases from 1.57 for NL-ZSM-5 to 0.91 for ZSM-5-C (Table 3), which has a higher fraction of Brønsted sites. This favors protonation and alkylation routes that yield readily desorbed, light alkyl-aromatics, while suppressing dehydrogenation-condensation pathways on Lewis acid sites associated with extra-framework aluminum, thereby reducing the formation of highly unsaturated polyaromatic coke precursors. At the same time, the relocation of strong acid sites cooperates with the hierarchical pore network in regulating both adsorption strength and residence time. Molecular simulations show that micropores provide the strongest adsorption environment for benzene, whereas mesopores have weaker adsorption enthalpies but much higher diffusion coefficients. When strong acid sites are concentrated in micropores, the combination of strong adsorption and severe confinement leads to long residence times and high local concentrations, which promotes deep dehydrogenation and condensation. After TEOH treatment, a larger fraction of strong acid sites is situated on mesoporous and external surfaces. In these more open regions, the weaker confinement and faster diffusion shorten the residence time of benzene derived intermediates at strong acid sites, thereby reducing their probability of evolving into polyaromatic coke and slowing down catalyst deactivation. Additionally, the micropore volume decreased from 0.11 to 0.05 cm³/g, representing a reduction of nearly 50%, which further compresses the physical space available for “micropore strong acid sites prone to inducing condensation.” This modification fundamentally diminishes the likelihood of carbon deposit precursor formation.

Molecular simulations indicate a significant increase in the diffusion coefficient of benzene at elevated temperatures (873 K). However, thermogravimetric analysis (TGA) results demonstrate a sharp increase in carbon deposition. This seemingly contradictory phenomenon may be attributed to the competition between reaction kinetics and mass transfer dynamics under high temperatures. According to the Arrhenius law, while higher temperatures improve molecular diffusivity, they exert a far stronger accelerating

effect on surface reaction rates, including protonation, dehydrogenation, and condensation. That is, at high temperatures, once a benzene molecule is adsorbed, the rate at which it undergoes a series of reactions to transform into a poorly desorbable coke precursor far exceeds its rate of diffusive escape. Consequently, coke deposition on the zeolite catalyst increases to 6.9% under these conditions. Therefore, the essence of high-temperature carbon deposition is the dominant role of ultra-fast surface reaction kinetics, whose negative impact completely overshadow the marginal positive effects brought by enhanced diffusion.

Based on the above discussion, it is evident that pore size and temperature are not isolated factors; rather, they function as interdependent regulators that co-govern the coking behavior of the catalyst. This study demonstrates that an optimized pore structure is key to resisting the negative effects of high temperatures. In the pure micropore catalyst (NL-ZSM-5), slow diffusion combined with rapid reactions at high temperatures resulted in the most severe coking (11.9%). In contrast, in the hierarchical catalyst (ZSM-5-C), the efficient diffusion channels allow effective molecular transport even at high temperatures, thereby significantly reducing residence time and thereby keeping the carbon deposition at a low level (4.12%).

In summary, this study concludes that the anti-deposition advantage of hierarchical ZSM-5 arises not only from the space-release effect contributed by mesopores, but more importantly from the synergistic regulation of “adsorption-diffusion” initiated by the restructuring of micropores and mesopores. This finding offers substantial guidance for the design of hierarchical catalysts. A deliberate modification strategy should incorporate adequate mesoporous networks to ensure superior diffusion properties while retaining essential micropores to sustain adsorption capacity, thus achieving an optimal balance between catalytic activity and stability.

3 Conclusion

This study demonstrates that the coking behavior of ZSM-5 zeolites is synergistically regulated by reaction temperature and pore structure. Under high temperature condition, the deep condensation of benzene molecules are governed by the surface reaction kinetics, which in turn result in increased coke formation. However, the hierarchical pore structure constructed through TEOH treatment effectively suppresses this process. Its anti-coking mechanism lies in mesoporous channels greatly enhance molecular diffusion efficiency, significantly shortening the residence time of reactants and products within the channels. Simultaneously, partial etching of micropores reduces the number of the strongly adsorbed sites that trigger deep reactions. This synergistic effect of “diffusion enhancement” and “adsorption site regulation” reduced the coking amount of ZSM-5-C with the most developed

mesopores to 4.12%, only one-third of that on the pure micropore sample (11.9%).

In summary, this study reveals the competitive mechanism of “adsorption-diffusion-reaction” in the carbon deposition process at the molecular level. The anti-coke depositing advantage of hierarchical porous ZSM-5 does not stem from a simple increase in traditional pore volume, but rather from its optimized control over the critical parameter of molecular residence time. This discovery provides a clear theoretical guidance for designing high-performance anti-coke depositing catalysts. An ideal catalyst should construct a sufficiently unobstructed mesoporous network while retaining necessary active sites, thereby achieving an optimal balance between mass transfer efficiency and reaction activity.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] YANG X, SU X, CHEN D, et al. Direct conversion of syngas to aromatics: A review of recent studies[J]. *Chin J Catal*, 2020, 41: 561–573.
- [2] YANG L, LIU Z, LIU Z, et al. Correlation between H-ZSM-5 crystal size and catalytic performance in the methanol-to-aromatics reaction[J]. *Chin J Catal*, 2017, 38(5): 683–690.
- [3] LIU Y, SUN M, YAO Q, et al. Advancements, mechanisms, and challenges in the catalytic conversion of coal, coal tar, model compounds, and coal+x: An in-depth analysis of light aromatics preparation and future perspectives[J]. *Fuel*, 2025, 385: 134094.
- [4] GU S, YAN S, FENG J, et al. Pressurized hydrogasification and cobalt-catalyzed hydrogasification behaviors of naphthalene as a coal-based model compound[J]. *J Anal Appl Pyrolysis*, 2024, 183: 106773.
- [5] QIAO X, WANG X, TAN C, et al. Precious metals catalyze the saturated hydrogenation of polycyclic aromatic hydrocarbons in coal tar[J]. *Catalysts*, 2025, 15(4): 397.
- [6] CHEN N Y, GARWOOD W E. Industrial application of shape-selective catalysis[J]. *Catal Rev Sci Eng*, 1986, 28(2/3): 185–264.
- [7] WEI L, WANG H, DONG Q, et al. A review on the research progress of zeolite catalysts for heavy oil cracking[J]. *Catalysts*, 2025, 15(4): 401.
- [8] XUE D, LIU R, FENG Z, et al. Tailoring of Pt particle density on the surface of dealuminated ZSM-5 and its hexane cracking performance[J]. *J Fuel Chem Technol*, 2025, 53(12): 1789–1797.
- [9] MI Y, YU X, PU X, et al. Modified ZnZrO_x coupled with ZSM-5 as the catalyst for the hydrogenation of CO₂ to aromatics[J]. *J Fuel Chem Technol*, 2025, 53(7): 1038–1049.
- [10] DU S, GAMLIEL D P, GIOTTO M V, et al. Coke formation of model compounds relevant to pyrolysis bio-oil over ZSM-5[J]. *Appl Catal A: Gen*, 2016, 513: 67–81.
- [11] BRANDANI S, JAMA M, RUTHVEN D. Diffusion, self-diffusion and counter-diffusion of benzene and p-xylene in silicalite[J]. *Microporous Mesoporous Mater*, 2000, 35–36: 283–300.
- [12] LIU X, ZHAO Z, TANG M, et al. Study of pre-coking modified ZSM-5 molecular sieve and its benzene and syngas alkylation properties[J]. *J Fuel Chem Technol*, 2024, 52(10): 1516–1528.
- [13] MENG X, LIN C, ZHANG Y, et al. Mass transfer behavior of benzene in hierarchically structured ZSM-5[J]. *Front Chem*, 2019, 7: 502.
- [14] PEREZ-RAMIREZ J, CHRISTENSEN C H, EGEHLAD K, et al. Hierarchical zeolites: Enhanced utilisation of microporous crystals in catalysis by advances in materials design[J]. *Chem Soc Rev*, 2008, 37(11): 2530–2542.
- [15] BENSFAFI B, CHOUAT N, DJAFRI F. The universal zeolite ZSM-5: Structure and synthesis strategies – A review[J]. *Coord Chem Rev*, 2023, 496: 215397.
- [16] DITTMANN D, KAYA E, DYBALLA M. Desilicated ZSM-5 catalysts: Properties and ethanol-to-aromatics (ETA) performance[J]. *ChemCatChem*, 2023, 15(20): 1–12.
- [17] ABELLÓ S, BONILLA A, PÉREZ-RAMÍREZ J. Mesoporous ZSM-5 zeolite catalysts prepared by desilication with organic hydroxides and comparison with NaOH leaching[J]. *Appl Catal A: Gen*, 2009, 364(1): 191–198.
- [18] LI S, LU B, WANG Y, et al. Dealkylation properties of alkylphenols over hierarchical ZSM-5 synthesized by desilication with TPAOH[J]. *Fuel Process Technol*, 2023, 246: 107759.
- [19] ZHANG Y, LI M, XING E, et al. Protective desilication of highly siliceous H-ZSM-5 by sole tetraethylammonium hydroxide for the methanol-to-propylene (MTP) reaction[J]. *RSC Adv*, 2018, 8(66): 37842–37854.
- [20] GROEN J C, JANSEN J C, MOULIJN J A, et al. Optimal aluminum-assisted mesoporosity development in MFI zeolites by desilication[J]. *J Phys Chem B*, 2004, 108(35): 13062–13065.
- [21] ESCHENBACHER A, GOODARZI F, SARAEIAN A, et al. Performance of mesoporous HZSM-5 and Silicalite-1 coated mesoporous HZSM-5 catalysts for deoxygenation of straw fast pyrolysis vapors[J]. *J Anal Appl Pyrolysis*, 2020, 145: 104712.
- [22] ZHAO J, CAO J, WEI F, et al. Acidity-controlled hollow HZSM-5 for lignite pyrolysis volatiles valorization to light aromatics[J]. *Chem Eng Sci*, 2024, 292: 120003.
- [23] GORZIN F, TOWFIGHI DARIAN J, YARIPOUR F, et al. Preparation of hierarchical HZSM-5 zeolites with combined desilication with NaAlO₂/tetrapropylammonium hydroxide and acid modification for converting methanol to propylene[J]. *RSC Adv*, 2018, 8: 41131–41142.
- [24] KARPE S, VESER G. Coke formation and regeneration during Fe-ZSM-5-catalyzed methane dehydro-aromatization [J]. *Catalysts*, 2024, 14(5): 292.
- [25] WEISSENBERGER T, MACHOKE A G F, BAUER J, et al.

- Hierarchical ZSM-5 catalysts: The effect of different intracrystalline pore dimensions on catalyst deactivation behaviour in the MTO reaction[J]. *ChemCatChem*, 2020, 12(9): 2461–2468.
- [26] HE S, GOLDHOORN H R, TEGUDEER Z, et al. A time- and space-resolved catalyst deactivation study on the conversion of glycerol to aromatics using H-ZSM-5[J]. *Chem Eng J*, 2022, 434: 134620.
- [27] SCHMIDT F, HOFFMANN C, GIORDANINO F, et al. Coke location in microporous and hierarchical ZSM-5 and the impact on the MTH reaction[J]. *J Catal*, 2013, 307: 238–245.
- [28] KALANTZOPOULOS G N, ROJO G D, PAPPAS D K, et al. Real-time regeneration of a working zeolite monitored via operando X-ray diffraction and crystallographic imaging: How coke flees the MFI framework[J]. *Dalton Trans*, 2022, 51(44): 16845–16851.
- [29] GOETZE J, YARULINA I, GASCON J, et al. Revealing lattice expansion of small-pore zeolite catalysts during the methanol-to-olefins process using combined operando X-ray diffraction and UV-vis spectroscopy[J]. *ACS Catal*, 2018, 8(3): 2060–2070.
- [30] BORODINA E, SHARBINI HARUN KAMALUDDIN H, MEIRER F, et al. Influence of the reaction temperature on the nature of the active and deactivating species during methanol-to-olefins conversion over H-SAPO-34[J]. *ACS Catal*, 2017, 7(8): 5268–5281.
- [31] NORDVANG E C, BORODINA E, RUIZ-MARTINEZ J, et al. Effects of coke deposits on the catalytic performance of large zeolite H-ZSM-5 crystals during alcohol-to-hydrocarbon reactions as investigated by a combination of optical spectroscopy and microscopy[J]. *Chem Eur J*, 2015, 21(48): 17324–17335.
- [32] YUNG M M, STARACE A K, GRIFFIN M B, et al. Restoring ZSM-5 performance for catalytic fast pyrolysis of biomass: Effect of regeneration temperature[J]. *Catal Today*, 2019, 323: 76–85.
- [33] AN H, ZHANG F, GUAN Z, et al. Investigating the coke formation mechanism of H-ZSM-5 during methanol dehydration using operando UV-Raman spectroscopy[J]. *ACS Catal*, 2018, 8(10): 9207–9215.
- [34] FAN S, WANG H, WANG P, et al. Formation and evolution of the coke precursors on the zeolite catalyst in the conversion of methanol to olefins[J]. *Chem Catal*, 2024, 4(4): 100927.
- [35] NIKOLOPOULOS N, VEENHUIZEN O, WECKHUYSEN B M. Effect of steaming on waste-derived zeolite ZSM-5 as methanol-to-hydrocarbons catalyst [J]. *ChemCatChem*, 2022, 14(21): 1-12.
- [36] WANG C, BRENIG A, XU J, et al. Evidence of preferential aluminum site loss during reaction-induced dealumination [J]. *J Am Chem Soc*, 2024, 146(50): 34279–34284.
- [37] BROGAARD R Y, WECKHUYSEN B M, NØRSKOV J K, et al. Guest-host interactions of arenes in H-ZSM-5 and their impact on methanol-to-hydrocarbons deactivation processes [J]. *J Catal*, 2013, 300: 235–241.
- [38] BU L, NIMLOS M R, ROBICHAUD D J, et al. Diffusion of aromatic hydrocarbons in hierarchical mesoporous H-ZSM-5 zeolite[J]. *Catal Today*, 2018, 312: 73–81.
- [39] LIU Q, HE P, QIAN X, et al. Enhanced CO₂ adsorption performance on hierarchical porous ZSM-5 zeolite[J]. *Chin J Catal*, 2017, 31(12): 13933–13941.
- [40] DEROUANE E G, CHANG C D. Confinement effects in the adsorption of simple bases by zeolites[J]. *Microporous Mesoporous Mater*, 2000, 35–36: 425–433.

孔结构与温度协同调控多级孔 ZSM-5 分子筛在苯催化中的积炭特性研究

曾庆洲¹, 韩雪峰², 赵洪宇³, 李吉辉⁴, 柳树成^{1,2,*}

(1. 辽宁工程技术大学 矿业学院, 辽宁 阜新 123000; 2. 辽宁工程技术大学 鄂尔多斯研究院, 内蒙古 鄂尔多斯 017004;

3. 北京科技大学 资源与安全工程学院, 北京 100083; 4. 中国矿业大学(北京) 化学与环境工程学院, 北京 100083)

摘要: 传质限制引起的积炭是传统微孔 ZSM-5 沸石在煤焦油催化裂解过程中的一个关键挑战。本研究选择苯作为煤焦油的模型化合物, 采用四乙基氢氧化铵 (TEAOH) 对原始 ZSM-5 (NL-ZSM-5) 进行改性, 制备了具有不同介孔尺寸的多级孔 ZSM-5 沸石。通过 XRD、FT-IR、BET 和 TEM 等多尺度表征技术, 结合固定床实验和分子模拟, 研究了孔结构、酸性性质和反应温度对沸石积炭机理的影响。表征结果表明, 通过 TEAOH 选择性脱硅成功引入了介孔, 同时保留了 ZSM-5 的 MFI 拓扑结构。当 TEAOH 浓度为 0.4 mol/L 时 (ZSM-5-C), 总孔容从 0.24 cm³/g 增加到 0.43 cm³/g, B 酸量从 0.28 mmol/g 增加到 0.67 mmol/g, 且酸位点可及性显著提高。催化反应和积炭分析表明, 多级孔结构通过“扩散增强 - 吸附位点调控”的协同效应抑制积炭。ZSM-5-C 的积炭量为 4.0%, 仅为纯微孔 NL-ZSM-5 (11.9%) 的三分之一。分子动力学模拟结果证实, 苯分子在 3.0 nm 介孔模型中的扩散系数比在 2.0 nm 模型中提高了一个数量级。此外, 吸附容量随介孔尺寸增加而降低, 这也缩短了分子在孔道中的停留时间。研究还发现, 尽管升高温度可增强分子扩散速率, 但表面缩合反应的指数增长将主导积炭形成, 而多级孔结构能有效缓解这一负面影响。本研究为煤焦油转化高效抗积炭催化剂的设计提供了理论基础和技术参考。

关键词: 多级孔 ZSM-5 沸石; 四乙基氢氧化铵 (TEAOH) 改性; 苯催化转化; 积炭调控; 分子模拟 (蒙特卡洛/分子动力学)

中图分类号: TQ426.8; TQ51

文献标识码: A

作者简介:



曾庆州(2000), 辽宁工程技术大学在读硕士研究生, 研究方向为多级孔 ZSM-5 分子筛改性及其在煤焦油催化转化中的应用, z1905467322@163.com。



柳树成(1987), 博士, 副教授, 研究方向为低阶煤热化学转化制备精细化学品及低阶煤浮选药剂设计与应用, lsc33884287@163.com。