

Acid-metal modified HZSM-5 catalyst for methanol aromatization

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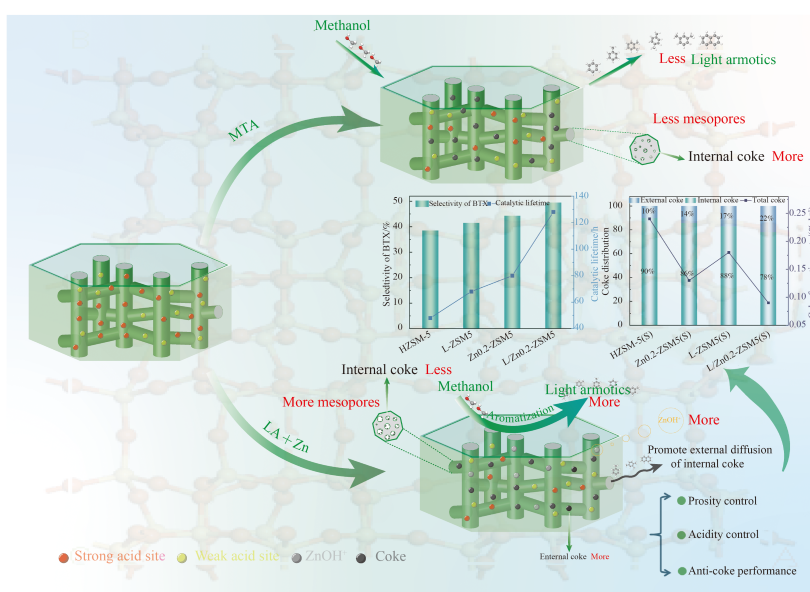
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Abstract: The HZSM-5 zeolite was co-modified with levulinic acid (LA) and Zn to obtain L/Zn0.2-ZSM5. Comprehensive characterization was conducted using XRD, N₂ adsorption-desorption, NH₃-TPD, Py-FTIR, Raman, XPS and TGA to investigate the effects of co-modification on the catalyst's structure, physicochemical properties, catalytic performance, and coke-deposition behavior. The results indicate that L/Zn0.2-ZSM5 possesses a specific surface area comparable to that of HZSM-5, while exhibiting significantly larger pore volume and average

pore size than HZSM-5 and the singly modified catalysts (L-ZSM5 and Zn0.2-ZSM5). In addition, co-modification markedly decreases the total acid amount and acid strength, while establishing a moderate Brønsted-to-Lewis (B/L) acid ratio. These structural and acidic modifications endow L/Zn0.2-ZSM5 with a BTX (benzene, toluene, xylene) selectivity of 58.75% and a catalytic lifetime of 128 h, both of which surpass those of the singly modified catalysts and those with different Zn loadings. The enhanced catalytic performance of L/Zn0.2-ZSM5 correlates with its significantly lower proportion of internal coke and greater coke storage capacity compared with the unmodified and singly modified catalysts. This behavior is attributed to the co-modification-induced pore enlargement, which effectively reduces the diffusion resistance of coke precursors and suppresses the graphitization process of coke. Furthermore, LA strengthens the interaction between Zn species and the zeolite framework, promotes Zn dispersion, and substantially increases the proportion of [ZnOH]⁺ species to 61.36%.

Key words: HZSM-5; levulinic acid; Zn; synergistic modification; MTA selectivity; coke



The methanol to aromatics (MTA) process represents an important non-petroleum-based route for aromatic synthesis and exhibits remarkable potential for sustainable development. Methanol, the feedstock for this process, can be produced from diverse resources, including biomass, natural gas, coal, and even CO₂^[1-2]. HZSM-5 zeolite has

been widely applied in MTA reactions due to its high specific surface area, tunable acidity and unique microporous structure. However, conventional HZSM-5 catalysts still suffer from intrinsic limitations, such as relatively low selectivity toward BTX (benzene, toluene, and xylene) and pronounced susceptibility to deactivation

Received: 2025-12-05; Revised: 2026-01-26

Foundation items: Supported by Science and Technology Project of Liaoning Province (20170540585).

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DOI: 10.1016/S1872-5813(26)60705-0 CSTR: 32157.14.2097-213X.2026.JFCT.0064 Associated Data DOI: 10.57760/sciencedb.j00124.00420

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caused by coke formation, which hinder the industrial application of the MTA process.

To address these technical bottlenecks, researchers have explored various modification strategies, including acid treatment, alkali treatment, metal loading, and hydrothermal treatment. Nevertheless, each single modification approach exhibits distinct drawbacks. For instance, acid or alkali treatment can improve mass transfer properties but often results in the loss of acid sites, thereby limiting aromatic selectivity^[3]. Metal modification (e.g., with Zn, Ga, Ca) increases aromatization activity, but achieving both high aromatic selectivity and long catalyst lifetime simultaneously remains challenging^[4]. Hydrothermal treatment can improve stability and suppress coke formation, yet it normally compromises initial reaction activity due to the depletion of strong acid sites^[5].

In recent years, synergistic modification strategies involving multiple components have demonstrated remarkable advantages. Approaches, such as regulating Zn dispersion *via* trace Ca incorporation^[6], promoting Ga dispersion by constructing hollow mesoporous structures *via* alkali treatment^[7], and optimizing acidity and pore structure *via* steam treatment^[8], have all achieved remarkable improvements in catalytic performance. To date, synergistic modification studies have predominantly focused on bimetallic modification^[6,9–11], alkali-metal composite modification^[12], and steam-metal modification^[13], whereas investigations into acid-metal synergistic modification remain relatively scarce.

Our research group has previously employed levulinic acid (LA) and Zn to individually modify HZSM-5. LA enables the precise construction of micro-meso hierarchical pore channels while preserving the integrity of the zeolite framework, thereby improving molecular diffusion performance. Meanwhile, a low Zn loading (<1%) enhances the interaction between Zn and framework aluminum, promotes the formation of $[\text{ZnOH}]^+$ active sites, and strengthens the dehydroaromatization process. Herein, this study focuses on an LA-Zn synergistic modification strategy. Through systematic structural characterization and catalytic performance evaluation, we aim to elucidate the synergistic mechanism among pore structure, acidity, and active sites, thereby providing experimental insights and practical guidance for the development of high-performance MTA catalysts.

1 Experimental

1.1 Preparation of the parent HZSM-5

The preparation of HZSM-5 follows the procedures reported in the prior study^[4].

1.2 Modification of HZSM-5

HZSM-5 molecular sieve was added to a 1% LA solution

with a HZSM-5 to LA solution mass ratio of 1:40. The mixture was stirred at 40 °C for 24 h, followed by the hydrothermal treatment at 160 °C for 12 h in a hydrothermal reactor. After cooling down, the resulting material was washed with deionized water until reaching a neutral pH. The material was then dried at 100 °C for 12 h before calcination at 550 °C for 4 h. The resulting catalyst is designated as L-ZSM5.

Zn incorporation over HZSM-5 is described below. A specific amount of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solid (corresponding to a Zn loading of 0.2%) was dissolved in water. HZSM-5 (Si/Al = 61) was then added to the previously prepared solution *via* an equal-volume impregnation method. The mixture was then aged at room temperature for 12 h before drying and calcination following the procedures described above, yielding Zn0.2-ZSM5.

Zn incorporation over L-ZSM5 followed the modification approach described above and yielded synergistically modified L/Zny-ZSM5 catalysts (where *y* represents the Zn loading: *y* = 0.1%, 0.2%, 0.6%, 2.0%).

1.3 Catalyst characterization

X-ray diffraction (XRD) patterns were collected on a D/max-R diffractometer using Cu $K\alpha$ radiation (40 kV, 15 mA), ranging from 5° to 70° with a scanning rate of 8(°)/min and a step size of 0.01°.

N_2 physisorption isotherms were characterized at 77 K using an ASAP 2010 adsorption analyzer. Before measurement, approximately 100 mg of the catalyst was degassed under vacuum at 250 °C for 6 h. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, while the micropore surface area and micropore volume were determined by the *t*-plot method. The pore size distribution was evaluated using the nonlocal density functional theory (NLDFT) model.

NH_3 -TPD profiles were obtained using an AutoChem II 2920 chemisorption analyzer. 200 mg of the catalyst in a U-shaped quartz tube was pretreated in a He atmosphere at 600 °C (ramping rate of 20 °C/min) for 30 min. After cooling down to 100 °C, 15% NH_3 /He mixture flow rate (40 mL/min) was introduced for adsorption. After 30 min, the mixture was switched to high-purity He purging for 15 min, followed by heating at 10 °C/min to 650 °C while recording signals using TCD.

Pyridine adsorption infrared (Py-FTIR) spectroscopy was conducted on a Vertex 70 spectrometer. Prior to testing, 20 mg of the catalyst was placed in a pyridine adsorption cell and treated at 400 °C for 2 h under a vacuum of 2.5×10^{-2} Pa. After cooling down to room temperature, the temperature was raised to 150 °C and held for 1 h before collecting the infrared spectrum. Based on the absorbance of the characteristic pyridine infrared peaks and their corresponding molar extinction coefficients, combined with the material mass and peak area, the amounts of Brønsted acid and Lewis acid were calculated to determine their content and distribution ratio.

X-ray photoelectron spectra (XPS) were collected using an ESCALAB 250 X-ray photoelectron spectrometer. The X-ray source was Al-K α radiation, with the lens mode set to Large Area XL and a beam spot diameter of 650 μ m. The pass energies for full-spectrum and narrow-spectrum scans were 200 and 30 eV, respectively, in constant analyzer energy (CAE) mode. The acquired spectra were calibrated using the C 1s peak at a binding energy of 284.8 eV.

Thermogravimetric analysis (TGA) was performed using a Q600 instrument to analyze the coke deposition on deactivated catalysts. The TGA test was conducted in an air atmosphere. 10 mg of the catalyst was placed in an Al₂O₃ crucible and heated to 800 °C at a rate of 10 °C/min, followed by cooling to room temperature at 25 °C/min. The mass change of the sample during this process was recorded.

Fourier transform infrared (FT-IR) spectra were recorded using a WQF-510 spectrometer in the wavenumber range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹. The materials were thoroughly mixed with KBr at a mass ratio of 1:200 and pressed into pellets for analysis. A background spectrum of pure KBr was collected prior to each measurement to eliminate background interference.

Raman spectra were collected using a DXR3 Raman spectrometer (Thermo Fisher Scientific, USA). The measurements were performed with a 532 nm laser over a spectral range of 100–2000 cm⁻¹, using a laser power of 1% and an acquisition time of 50 s.

1.4 Catalytic performance evaluation

The methanol aromatization reaction performance was evaluated using a self-made fixed-bed reactor. The reaction tube measured 500 mm $\times$ 6 mm, with a catalyst loading of 1.40 g (20–40 mesh). The reaction conditions were set at a temperature of 420 °C, a weight hourly space velocity (WHSV) of 1.24 h⁻¹ and a pressure of 0.6 MPa. Samples were collected every 2 h. Prior to methanol feeding, the catalyst was activated at 450 °C for 25 min under N₂ flow (8.82 mL/min). The oil-phase and aqueous-phase products were analyzed using an SP-1000 gas chromatograph. The oil-phase products were analyzed with an FID detector and a KB-17 capillary column (50 m $\times$ 0.25 mm $\times$ 0.5 μ m). The aqueous-phase products were analyzed using an OV-101 capillary column (inner diameter 0.25 mm) and a TCD detector. The gaseous products were analyzed using a GC-4000A chromatograph equipped with an FID detector and a capillary column packed with HJ-Al₂O₃/S.

1.5 Product calculation

$$x_T = \frac{m_{in} - m_{out}}{m_{in}} \times 100\% \quad (1)$$

$$Y_{oil} = \frac{m_{oil}}{m_{in} - m_{out}} \times 100\% \quad (2)$$

$$s_i = \frac{n_i}{\sum n_i} \times 100\% \quad (3)$$

where x_T , m_{in} and m_{out} denote the methanol conversion (%), inlet methanol mass (g) and outlet methanol mass (g), respectively; Y_{oil} and m_{oil} denote the oil-phase product yield (%) and the mass of oil-phase products (g), respectively; s_i and n_i represent the selectivity of product i (%) and the moles of carbon of product i among all collected products, respectively.

1.6 Calculation of carbon deposit

$$W_{in} = (v_{micro, fresh} - v_{micro, spent}) \times \rho_{coke} \times 100\% \quad (4)$$

$$W_{out} = (W_{coke} - W_{in}) \times 100\% \quad (5)$$

where W_{in} , W_{out} , W_{coke} represent internal coke quantity (%), external coke quantity (%) and total coke quantity (%), respectively; $v_{micro, fresh}$ and $v_{micro, spent}$ are the pore volumes per unit mass of the catalyst before and after deactivation (cm³/g), respectively; ρ_{coke} is the density of coke, taken as 1.22 g/cm³[14].

$$W_{coke} = W_{200} - W_{800} \quad (6)$$

$$W_s = W_{200} - W_{500} \quad (7)$$

$$W_H = W_{500} - W_{800} \quad (8)$$

$$Y = \frac{W_{in}}{W_{coke}} \times 100\% \quad (9)$$

$$v = \frac{W_{coke}}{t} \quad (10)$$

where W_{200} , W_{500} and W_{800} are percentages of the material mass relative to the initial mass at 200, 500 and 800 °C, respectively (%). W_s and W_H represent the amounts of soft coke (%) and hard coke (%), respectively. Y , t and v represent the percentage of internal coke relative to the total coke amount (%), the catalyst time-on-stream (h) and the average coke formation rate (%/h), respectively.

2 Results and discussion

2.1 Physicochemical properties of modified catalysts

2.1.1 Physical structure analysis

Figure 1 presents the XRD patterns of HZSM-5-based catalysts modified by different methods. The characteristic diffraction peaks of L-ZSM5, Zn0.2-ZSM5 and L/Zn0.2-ZSM5 at 2θ of 7.90°, 8.78°, 23.04°, 23.80° and 24.41° are consistent with those of pristine HZSM-5, indicating that the modification procedures did not disrupt the MFI topology of the zeolite framework[15]. Compared with HZSM-5, the diffraction peaks of L-ZSM5 and L/Zn0.2-

ZSM5 at 2θ of 45.1° and 45.6° (see the insert in Figure 1) exhibit different degrees of shift toward lower angles, which can be attributed to the removal of aluminum species induced by LA treatment. In addition, no diffraction peaks corresponding to ZnO are observed at 2θ of 31.7° and 36.3° for Zn0.2-ZSM5 and L/Zn0.2-ZSM5, suggesting that Zn species are highly dispersed on the catalyst surface^[16].

Figure 2 shows the N_2 adsorption-desorption isotherms (a) and pore size distribution curves (b) of HZSM-5-based catalysts modified by different methods. All four catalysts exhibit typical Type I isotherms, suggesting the presence of predominantly microporous structures^[1]. However, hysteresis loops, appearing in the relative pressure range $p/p_0 > 0.8$, indicate the presence of mesoporous structures within the catalysts. Among them, the hysteresis loops for HZSM-5 and Zn0.2-ZSM5 may be related to intercrystalline mesopores formed by catalyst particle stacking.

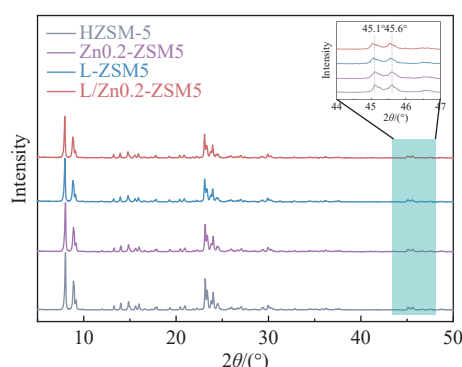


Fig. 1 XRD patterns of HZSM-5-based catalysts modified by different methods

The inset in Figure 1 shows enlarged XRD patterns in the 2θ range of 44.0° – 47.0° .

In contrast, the hysteresis loops for L-ZSM5 and L/Zn0.2-ZSM5 are significantly enhanced, suggesting that a significant amount of mesopores are generated due to the dealumination effect of LA. As shown in Figure 2(b), distinct mesoporous distribution peaks appear in the range of 3.0–4.0 nm for L-ZSM5 and L/Zn0.2-ZSM5, and the micropore peaks shift toward the mesoporous region, which may result from the enlargement or merging of some micropores.

Further analysis in conjunction with Table 1 shows that LA treatment increased the mesopore volume of HZSM-5 ($0.051 \text{ cm}^3/\text{g}$) to $0.151 \text{ cm}^3/\text{g}$ in L-ZSM5 and enlarged the average pore size from 0.90 to 3.39 nm. The substantial decrease in micropore-specific surface area also confirmed the transformation of micropores into mesopores. For Zn0.2-ZSM5, both the micropore specific surface area and pore volume decreased, which may be attributed to Zn species occupying and/or blocking part of the micropore space^[17]. Meanwhile, the introduction of Zn makes the catalyst particles fluffy and increases the intergranular mesopores generated by stacking, resulting in slightly higher mesopore volume and average pore size for Zn0.2-ZSM5 compared to HZSM-5.

Notably, after further introducing Zn onto L-ZSM5, the micropore volume increased from 0.103 to $0.152 \text{ cm}^3/\text{g}$, and the micropore specific surface area rose from 229 to $328 \text{ m}^2/\text{g}$. This phenomenon may originate from two aspects. First, the mesoporous structure introduced by LA enhances the distribution ratio of Zn species within the mesopores, mitigating blockage of micropores by Zn species. Second, Zn loading may redisperse or redistribute the deposits on the LA-modified material surface, as a result, re-exposing the previously obscured micropores. In addition, the mesopore volume of L/Zn0.2-ZSM5 ($0.240 \text{ cm}^3/\text{g}$) significantly exceeded that of the singly modified catalysts, which is roughly 4.7 times higher than that of HZSM-5.

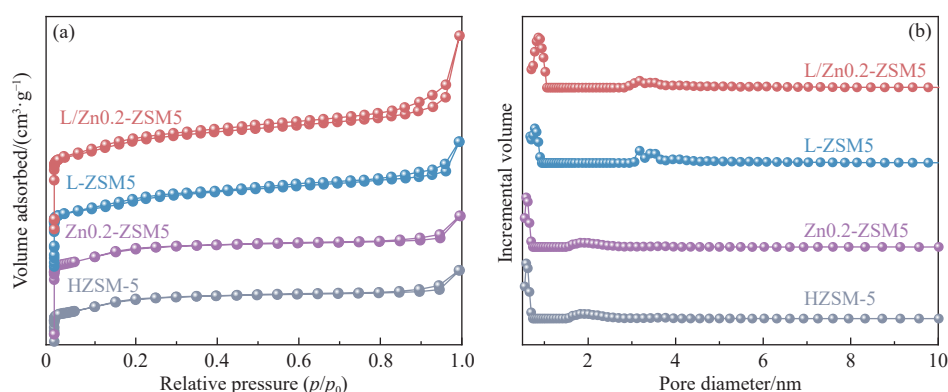


Fig. 2 (a) N_2 adsorption-desorption isotherm and (b) pore size distribution of HZSM-5-based catalysts

Table 1 Pore structure parameters of HZSM-5-based catalysts modified by different methods

Catalyst	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$S_{\text{micro}}/(\text{m}^2 \cdot \text{g}^{-1})$	$v_{\text{total}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$v_{\text{micro}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$v_{\text{meso}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$d_{\text{pore}}/\text{nm}$
HZSM-5	408	377	0.191	0.140	0.051	0.90
Zn0.2-ZSM5	392	361	0.209	0.133	0.076	1.03
L-ZSM5	299	229	0.253	0.103	0.151	3.39
L/Zn0.2-ZSM5	407	328	0.392	0.152	0.240	3.85

S_{BET} : BET specific surface area; S_{micro} : micropore specific surface area; v_{total} : total pore volume; v_{micro} : microporous pore volume; v_{meso} : mesoporous pore volume; d_{pore} : average pore size.

2.1.2 Chemical properties analysis

Figure 3(a) presents the NH_3 -TPD profiles of HZSM-5-based catalysts modified by different methods. The NH_3 desorption peaks near 230 and 450 °C correspond to weak acid sites and strong acid sites, respectively^[18]. As shown in Table 2, the modified catalysts, compared to HZSM-5, exhibit lower amounts of weak acid sites, strong acid sites, and total acid sites. Zn0.2-ZSM5 exhibits a similar acid site distribution characteristic to HZSM-5, e.g., similar desorption temperatures, whereas the strong acid site desorption peak area decreases, which can be attributed to interaction between Zn and strong acid centers (forming $[\text{ZnOH}]^+$ species), thereby neutralizing part of the strong acid sites^[19]. In contrast, L-ZSM5 and L/Zn0.2-ZSM5 show essentially identical desorption peak shapes. Compared to the former two catalysts, all desorption peaks of the latter two shift toward lower temperatures and decrease in peak area. These changes are closely related to the dealumination effect of LA on the zeolite.

Combined with Figure 3(b), the types of acid sites in the HZSM-5 zeolite were further clarified. The characteristic peaks at 1450, 1550 and 1490 cm^{-1} are assigned to pyridine adsorbed peaks on Lewis (L) acid sites, Brønsted (B) acid sites, and on both Brønsted and Lewis acid sites, respectively^[20]. Data in Table 2 show that, compared with HZSM-5, the introduction of Zn species (Zn0.2-ZSM5) significantly reduced the B/L ratio of the catalyst, indicative of enhanced L acid content and reduced B acid content. This change is generally ascribed to interactions between Zn species and framework Al. For the LA-modified catalyst

(L-ZSM5), both B acid and L acid contents decreased, with a more pronounced reduction in L acid, leading to an increased B/L ratio. In the HZSM-5-based catalyst, B acidity normally originates from framework Al, while L acidity is often associated with extra-framework aluminum (EFAl) and framework defects^[21], indicating that LA selectively removes EFAl in the zeolite. After further loading Zn species on L-ZSM5, L/Zn0.2-ZSM5 exhibited enhanced L acid content and decreased the B acid content, allowing for further modulation of its B/L ratio.

Figure 4 shows XPS spectra of L/Zn0.2-ZSM5 and Zn0.2-ZSM5. As shown in the full XPS spectrum in Figure 4 (a), the Al 2p peak appears at 74.80 eV, which is positively shifted relative to the standard value of HZSM-5 (74.0 eV), indicating a strong interaction between Zn species and the zeolite framework Al. In addition, the O 1s and Zn 2p signals of L/Zn0.2-ZSM5 are noticeably more intense than those of Zn0.2-ZSM5, which can be attributed to the LA treatment that enhances the exposure of Zn species on the catalyst surface and promotes their coordination with the surrounding oxygen environment. In Figure 4(b), compared with Zn0.2-ZSM5, the Si 2p characteristic peak of L/Zn0.2-ZSM5 exhibits an increased intensity accompanied by a slight shift toward higher binding energy. This behavior is closely associated with the LA-induced dealumination process, which further exposes Si species on the surface, and thus strengthens the Si 2p signal. In addition, dealumination decreases the proportion of Si-O-Al structures, modifying the local chemical environment of Si atoms and resulting in a positive shift of the Si 2p binding energy^[22–23].

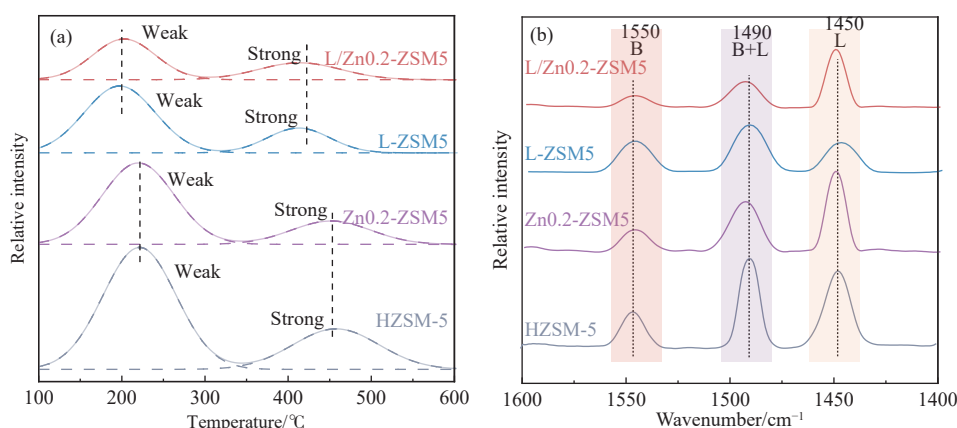


Fig. 3 (a) NH_3 -TPD, (b) Py-FTIR profiles of HZSM-5-based catalysts via different synthesis approaches

Table 2 Acidity results of HZSM-5-based catalysts modified by different methods

Catalyst	Acidity by strength ^a /(mmol·g ⁻¹)			Acidity by type ^b /(mmol·g ⁻¹)		
	weak	strong	total	Brønsted	Lewis	B/L
HZSM-5	0.536	0.347	0.883	0.361	0.564	0.640
Zn0.2-ZSM5	0.407	0.221	0.628	0.325	0.974	0.334
L-ZSM5	0.228	0.291	0.519	0.261	0.168	1.554
L/Zn0.2-ZSM5	0.263	0.166	0.429	0.197	0.359	0.549

^a: Density of the acid sites determined by NH_3 -TPD; ^b: Density of the acid sites determined by Py-FTIR.

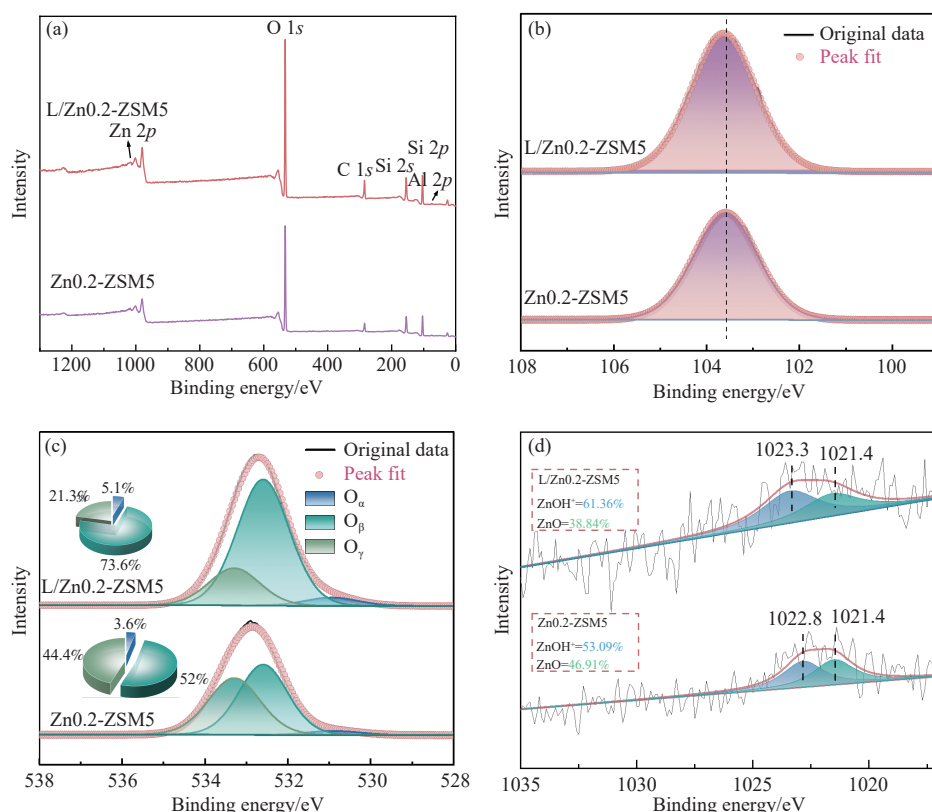


Fig. 4 XPS spectra of Zn0.2-ZSM5 and L/Zn0.2-ZSM5 catalyst: (a) Full spectrum diagram; (b) Si 2p; (c) O 1s; (d) Zn 2p_{3/2}

As shown in Figure 4(c), the O 1s spectrum can be deconvoluted into three components located at approximately 530.5, 532.0 and 533.5 eV, which are assigned to lattice oxygen (O_{α}), surface active oxygen (O_{β}), and surface adsorbed oxygen (O_{γ}), respectively^[24–25]. After LA treatment, the proportion of the O_{β} component increases markedly from 52.0% for Zn0.2-ZSM5 to 73.6% for L/Zn0.2-ZSM5. This enhancement is attributed to the increased population of catalytically active species ($[ZnOH]^+$) generated upon LA treatment, leading to a higher fraction of surface active oxygen, as further confirmed by the Zn 2p spectra (Figure 4(d)). The peaks located at 1021.4 and 1023.3 eV are assigned to ZnO and $[ZnOH]^+$ species, respectively, with the proportion of $[ZnOH]^+$ in L/Zn0.2-ZSM5 increasing from 53.09% to 61.36%.

This behavior can be explained by the selective removal of extra-framework aluminum (EFAI) species during LA treatment, which alleviates their shielding effect on surface bridging hydroxyl groups (Si-OH-Al) and thereby strengthens the coordination interaction between Zn^{2+} species and Si-OH-Al sites^[26–28]. Meanwhile, the mesoporous structure introduced by LA modification facilitates the migration of some surface ZnO species into the zeolite channels, enabling more effective interactions with acidic sites and further increasing the fraction of $[ZnOH]^+$ species^[29]. In addition, the binding energy of $[ZnOH]^+$ in L/Zn0.2-ZSM5 (1023.3 eV) is slightly higher than that in Zn0.2-ZSM5 (1022.8 eV), which can be attributed to LA-induced changes in the local chemical environment of Zn species, leading to stronger interactions between Zn^{2+} species and acidic sites^[20].

2.2 Effect of synergistic modification on catalytic performance

2.2.1 Comparison with single modification

Figure 5 shows the catalytic performances of the HZSM-5-based catalysts. As illustrated in Figure 5(a)–(c), the methanol conversion, oil-phase yield, and BTX selectivity of the different catalysts all follow the trend: L/Zn0.2-ZSM5 > Zn0.2-ZSM5 > L-ZSM5 > HZSM-5. Among them, the complete methanol conversion (e.g., 100% methanol conversion) time of the L/Zn0.2-ZSM5 catalyst was extended from 32 h for HZSM-5 to 104 h, and its catalytic lifetime increased to 128 h, which is significantly superior to that of the singly modified catalysts. Meanwhile, both oil-phase yield (11.62%) and BTX selectivity (58.76%) of the L/Zn0.2-ZSM5 are the highest among the tested catalysts. As shown in Figure 5(d), compared to the singly modified catalysts, the L/Zn0.2-ZSM5 catalyst exhibited a significant decrease in the selectivity of C_0-C_5 light alkanes and C_9+ heavy aromatics, whereas the selectivities of C_2-C_5 light olefins and BTX increased (the specific data are shown in Table 3). This is mainly attributed to the higher proportion of $[ZnOH]^+$ active species, which effectively promotes alkane dehydrogenation. Meanwhile, the lower amount of strong acid sites and the larger average pore size of L/Zn0.2-ZSM5 inhibit excessive alkylation of light aromatics and reduce diffusion resistance during the reaction.

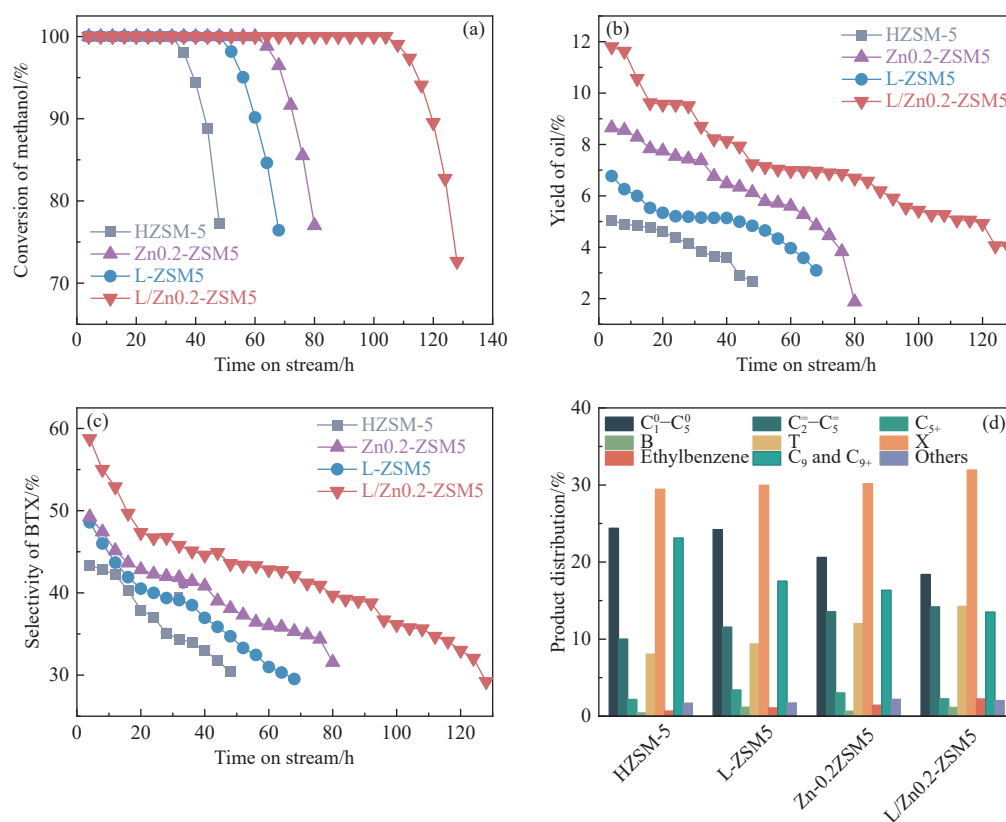


Fig. 5 (a) Methanol conversion, (b) oil phase yield, (c) BTX selectivity and (d) products distribution at the time on stream of 20 h of HZSM-5-based catalyst modified by different methods

Table 3 Products distribution of MTA reaction over different HZSM-5-based catalysts modified by different methods^a

Catalyst	Product distribution/%								
	C ₁ –C ₅	C ₂ –C ₅	C ₆ +	B	T	X	ethylbenzene	C ₉ and C ₉ +	others
HZSM-5	24.39	10.01	2.17	0.42	8.05	29.45	0.68	23.12	1.69
L-ZSM5	24.21	11.56	3.41	1.17	9.37	29.97	1.07	17.52	1.72
Zn0.2-ZSM5	20.61	13.56	3.03	0.65	12.02	30.17	1.43	16.34	2.19
L/Zn0.2-ZSM5	18.39	14.19	2.26	1.13	14.25	31.95	2.24	13.51	2.03

^a: Reaction conditions: 420 °C, 0.6 MPa, methanol WHSV 1.2 h⁻¹, TOS=20 h.

Furthermore, although the B/L ratio of L/Zn0.2-ZSM5 is not an extreme value, its BTX selectivity is the highest compared to the singly modified catalyst and the pristine HZSM-5 catalyst. This indicates that BTX selectivity is not solely governed by the B/L ratio but is the result of the synergistic regulation of multiple factors, including acid site distribution, the proportion of metal active species, and pore structure.

2.2.2 Effect of different Zn loadings

Figure 6 illustrates the effect of Zn loading on catalytic performance. Data in Figure 6(a)–(c) show that the catalyst with a Zn loading of 0.2% exhibits the highest lifetime, oil-phase yield, and BTX selectivity, whereas the catalyst with a Zn loading of 2.0% is the lowest among the catalysts investigated. In terms of catalysts with Zn loadings of 0.1% and 0.6%, the catalyst lifetime exhibits a reversed trend to

Zn content, whereas the oil-phase yield and BTX selectivity follow a linear trend. Data in Figure 6(d) show that Zn loading increase led to a steady rise in the yield of C₂–C₅ light olefins, which could be explained by the enhanced dehydrogenation effect *via* suppressing the conversion of olefins to alkanes. In contrast, BTX yield shows an initial increase followed by a decrease, whereas the C₉ heavy aromatics yield experienced a reversed trend. These results demonstrate that an optimal Zn loading facilitates the aromatization reaction. When the Zn loading is excessively high (e.g., 2.0%), strong acid sites are excessively weakened and accompanied by the loss of active species, thereby inhibiting the deep conversion of light hydrocarbons and the formation of aromatics. Simultaneously, excess Zn tends to block the pores, accelerating catalyst deactivation. On the other hand, when the Zn loading is too low (e.g., 0.1%), limited by the number of [ZnOH]⁺ active species, both the lifetime and

BTX selectivity are lower than those of L/Zn0.2-ZSM5. Overall, L/Zn0.2-ZSM5 with a Zn loading of 0.2%

demonstrates the optimal catalytic performance, with a catalytic lifetime of 128 h and a BTX selectivity of 58.75%.

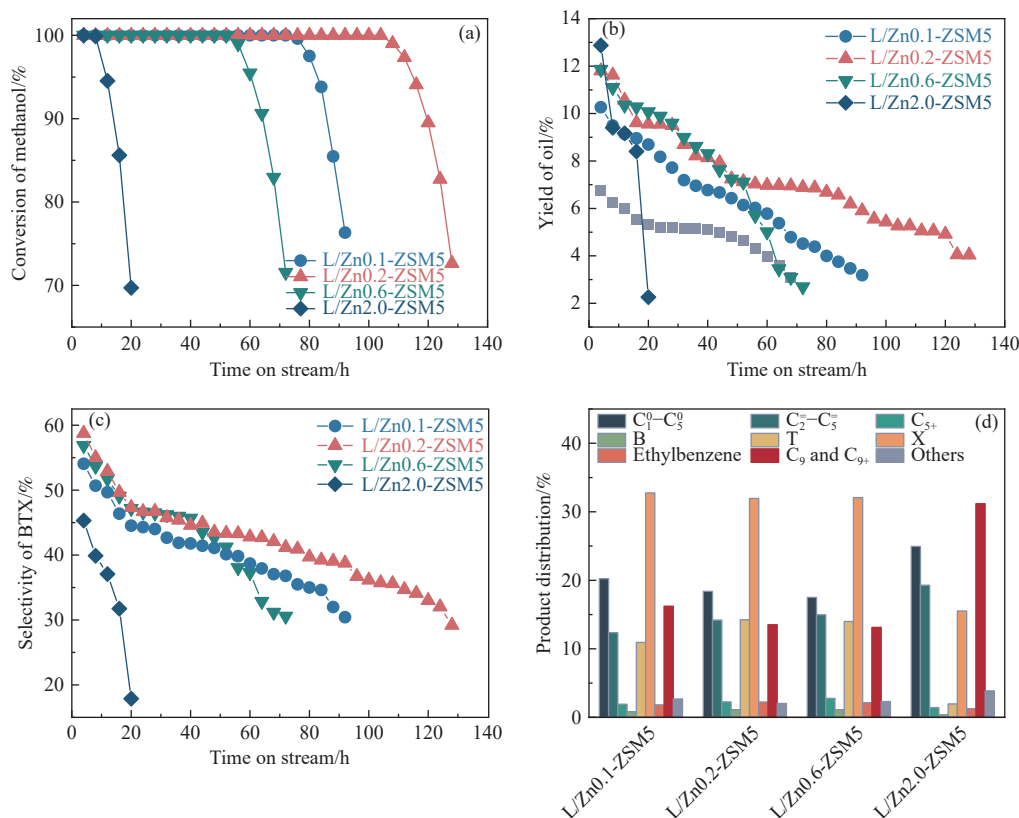


Fig. 6 (a) Methanol conversion, (b) oil phase yield, (c) BTX selectivity and (d) products distribution at the time on stream of 20 h of HZSM-5-based catalysts modified by different Zn loadings
Reaction conditions: 420 °C, 0.6 MPa, methanol WHSV 1.2 h⁻¹.

2.3 Effect of synergistic modification on coke formation

2.3.1 Influence on the crystalline structure of coke

Figure 7 compares the XRD patterns of the catalysts before and after reaction (catalysts after reaction were suffixed with (S) at the end of fresh catalyst names). Within the 2θ range of 5°–50°, all HZSM-5-based catalysts exhibit the characteristic diffraction peaks of the MFI topology, indicating that modification with LA and Zn and deactivation processing did not disrupt the zeolite framework structure. Figure 7(a) shows that the double peaks at 2θ of 23.1° and 23.3° observed in fresh catalysts merge into a single peak at 23.2° after deactivation, reflecting a transition of the unit cell from orthorhombic to tetragonal symmetry induced by coke deposition within the channels^[30–32]. Furthermore, the peak intensities of the deactivated catalysts at 2θ of 23.9°, 24.5°, 29.9° and 30.4° show significant changes, which can be attributed to local lattice distortion caused by intracrystalline coke^[33]; the slight shifts of the peaks at 23.9° and 30.4° toward higher angles may be related to lattice contraction resulting from partial removal of framework aluminum under high-

temperature and steam conditions^[34–35].

Furthermore, the diffraction peak at 2θ of 26.8° corresponds to the (002) crystal plane of graphitic coke, indicating partial graphitization of the coke during the deactivation process. Figure 7(b) shows that the ZnO diffraction peaks at 2θ of 36.1°, 34.4° and 32.1° are significantly enhanced in the deactivated sample^[36]. This is primarily attributed to the accumulation of coke, which weakens the interaction between $[\text{ZnOH}]^+$ species and the zeolite framework, promoting the transformation of $[\text{ZnOH}]^+$ into ZnO crystallites^[37–38]. In Figure 7(c), the double peaks of fresh ZSM-5 at 2θ of 45.5° (b -axis (0 10 0) plane) and 45.1° (a -axis (10 0 0) plane) merge into a single peak at 45.3° after deactivation. This suggests that coke deposition within the pores causes contraction of the unit cell along the a -axis and expansion along the b -axis^[31]. Additionally, the merged peak at 2θ of 45.3° and the graphitic carbon peak at 2θ of 26.8° for HZSM-5(S) are sharper than those for the modified samples, indicating that the modified HZSM-5 significantly inhibits coke formation. It is noteworthy that the double-peak splitting is most pronounced in the fresh sample of the co-modified catalyst L/Zn0.2-ZSM5, demonstrating that the synergistic effect between LA and Zn enhances the orthorhombic structural characteristics of the HZSM-5 zeolite.

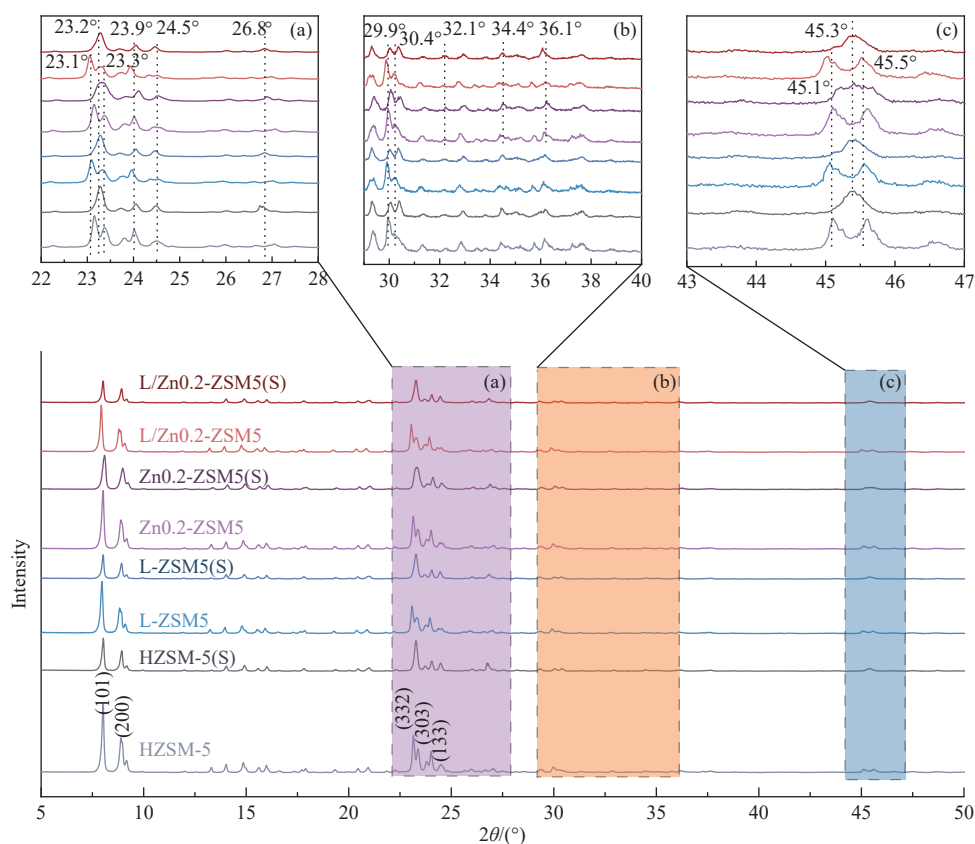


Fig. 7 XRD full spectra of the fresh and deactivated catalysts; ((a)–(c)) Enlarged views of the XRD patterns in the ranges of 22°–28°, 29°–40° and 43°–47° respectively

2.3.2 Influence on the chemical composition of coke

Figure 8 presents the FT-IR spectra of deactivated catalysts, revealing differences in carbonaceous deposits. Figure 8(a)–(b) shows that the 1300–1700 cm^{-1} and 2700–3150 cm^{-1} regions correspond to the characteristic absorption bands of aromatic and aliphatic compounds, respectively^[39–40]. The absorption peaks at 1372 and 1432 cm^{-1} are attributed to C–H bending vibrations of methyl and methylene groups, indicating monoalkyl-substituted aromatic hydrocarbons^[41]. The infrared absorption peak at 1538 cm^{-1} is associated with polyalkylbenzenes. The intensity of this peak is relatively low for Zn0.2-ZSM5(S) and L/Zn0.2-ZSM5(S), which is attributed to $[\text{ZnOH}]^+$ enhancing dehydrogenation and suppressing alkylation. The vibrational peak at 1597 cm^{-1} corresponds to the formation of polycyclic aromatic hydrocarbons (PAHs). HZSM-5(S) exhibits the strongest peak intensity at this position, indicating the coke on the HZSM-5 catalyst is predominantly composed of PAHs. PAHs can block micropores and cover active sites, potentially transforming into graphitic coke. In contrast, L/Zn0.2-ZSM5(S) shows significantly reduced peak intensity at 1597 cm^{-1} , demonstrating that the synergistic modification effectively inhibits PAH accumulation^[42]. In Figure 8(c), the 2700–3100 cm^{-1} region corresponds to C–H stretching vibration peaks. The absorption peaks at 2858 and 2969 cm^{-1} are assigned to symmetric and

asymmetric stretching vibrations of CH_3 , respectively, while the peak at 2930 cm^{-1} is assigned to the asymmetric stretching vibration of CH_2 ^[43]. The peak shapes and intensities in this region vary minimally among different ZSM-5 catalysts, suggesting similar aliphatic carbon deposit formation.

Figure 9 shows the Raman spectra of deactivated HZSM-5 catalysts. The characteristic peaks at 1179, 1375 and 1608 cm^{-1} are collectively attributed to the methylbenzenium carbocation (MB^+)^[44–46], while the peaks at 560, 727, 800 and 1408 cm^{-1} are associated with the PAHs species formed during the catalyst deactivation process^[43]. Analysis of the spectra indicates that the relative intensities of these characteristic peaks for the HZSM-5(S) sample are significantly higher than those of the other materials, suggesting a higher coke content and a coke structure more inclined toward graphitization. Furthermore, the C=C stretching vibration peak near 1608 cm^{-1} in HZSM-5(S) exhibits a slight redshift (shifting to 1603 cm^{-1}), further indicating that the coke species formed on HZSM-5(S) possess a higher degree of aromatic condensation and a greater tendency for graphitization^[47]. In contrast, for the synergistically modified L/Zn0.2-ZSM5(S) catalyst, the peak intensity at 1608 cm^{-1} is significantly reduced, and the characteristic peaks at 560, 727, 800 and 1408 cm^{-1} are almost invisible, demonstrating that the synergistic modification effectively suppresses the formation of hard coke during the reaction and exhibits excellent anti-coking performance.

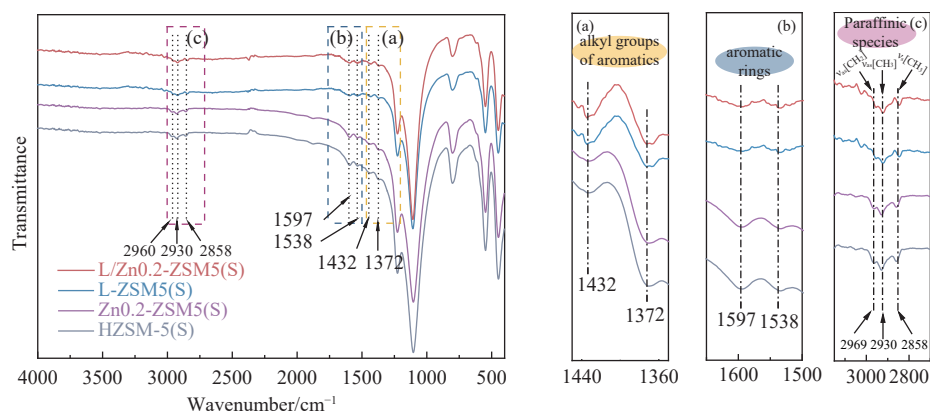


Fig. 8 FT-IR spectra of deactivated catalysts: (a) 1350–1450 cm^{-1} , (b) 1500–1650 cm^{-1} and (c) 2700–3150 cm^{-1}

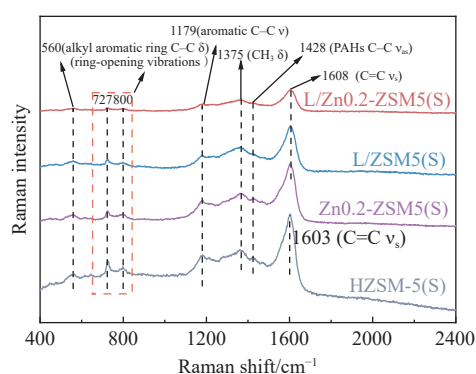


Fig. 9 Raman spectra for the deactivated HZSM-5 catalysts

2.3.3 Influence on the distribution of light and heavy coke

Figure 10 shows the distribution of light and heavy coke on HZSM-5-based catalysts modified by different methods. As shown in Figure 10(a), the DTG curves indicate that all deactivated catalysts exhibit two weight loss stages: the weight loss below 500 $^{\circ}\text{C}$ is mainly attributed to physical dehydration and the decomposition of light aromatics (soft coke), while the weight loss over 500 $^{\circ}\text{C}$ is primarily caused by the decomposition of polycyclic aromatic hydrocarbons with a low H/C ratio (hard coke)^[48–49]. For the co-modified catalyst L/Zn0.2-ZSM5(S), the coke content increases from 10.93% to 14.47% (Figure 10(b)), and the maximum weight loss peak shifts from 587.2 to 562.4 $^{\circ}\text{C}$. This indicates a decrease in the combustion temperature and thermal stability of its hard coke, along with an increase in the H/C ratio^[50].

Furthermore, as shown in Figure 10(c), (d), compared to HZSM-5(S), L-ZSM5(S) and Zn0.2-ZSM5(S), L/Zn0.2-ZSM5(S) exhibits a significant increase in soft coke content, along with the highest coke capacity (14.47%) and the lowest coke formation rate (0.09%/h), thereby substantially extending its catalytic lifetime. This performance enhancement is primarily attributed to two factors: the reduction of strong acid sites inhibits further alkylation of aromatics, while the increased mesoporous

structure promotes diffusion of coke precursors, alleviates microporous confinement, and results in a more porous coke structure.

2.3.4 Influence on the spatial distribution of coke

Figure 11 presents the N_2 adsorption-desorption characterization results of the HZSM-5-based catalysts after deactivation. As shown in Figure 11(a), the deactivated catalysts preserve a typical Type I isotherm, indicating that the deactivation process does not significantly alter the micropore-dominated adsorption behavior or destroy the MFI framework structure. However, the pore size distribution curves in Figure 11(b) reveal a pronounced decrease in the intensity of the micropore distribution peak for the deactivated catalyst, suggesting that coke deposition preferentially occurs within the micropore channels, leading to pore blockage and reduced micropore accessibility.

Figure 12 shows the spatial distribution of coke deposits over the deactivated catalysts. As illustrated in Figure 12(a), compared with HZSM-5(S), the modified catalysts Zn0.2-ZSM5(S), L-ZSM5(S) and L/Zn0.2-ZSM5(S) exhibit a reduction in both the proportion and formation rate of internal coke. In particular, the internal coke fraction of L/Zn0.2-ZSM5(S) decreased from 90% to 78%, while its internal coke formation rate reduced to 0.072 %/h. This is primarily attributed to the decrease of strong acid sites, which suppresses the formation of internal coke, while the enlarged pore size facilitates the outward diffusion of coke precursors, further inhibiting internal coke deposition. Since strong acid sites are mainly located within the micropores, even when the overall coke level is low, the impact of internal coke on catalyst deactivation remains significantly higher than that of external coke. Therefore, the deactivation behavior of the catalyst depends on the spatial distribution of coke (internal/external coke ratio) rather than the total amount of coke^[51]. Herein, although L/Zn0.2-ZSM5(S) possesses the highest total coke content, its lower proportion of internal coke and slower coking rate still endow it with a longer catalytic lifetime.

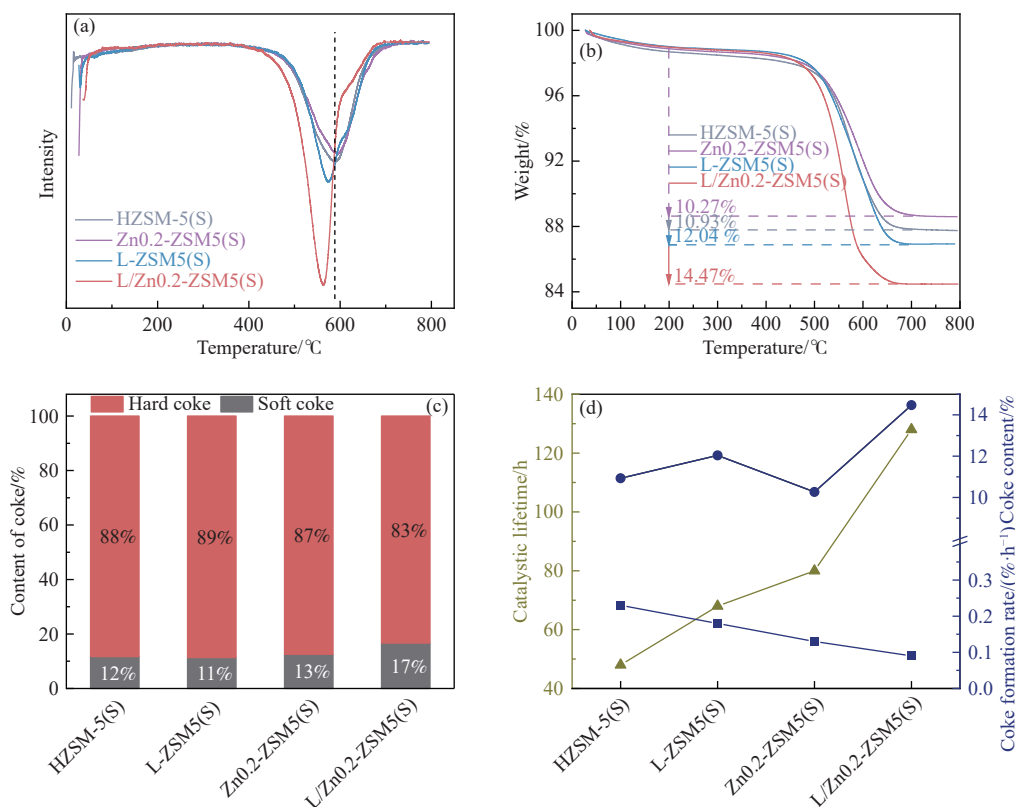


Fig. 10 (a) DTG curves, (b) TG curves, (c) soft and hard coke ratio and (d) coke deposition amount and average coke deposition rate of the deactivated catalysts

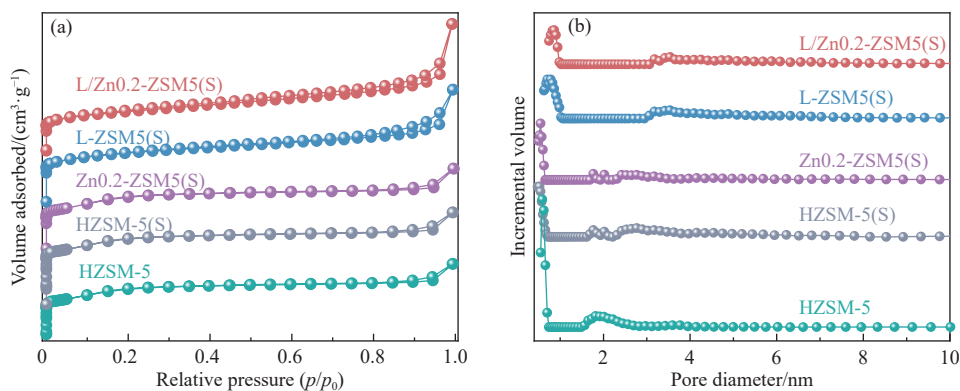


Fig. 11 (a) N₂ adsorption-desorption isotherms and (b) pore size distribution curves of the deactivated catalysts

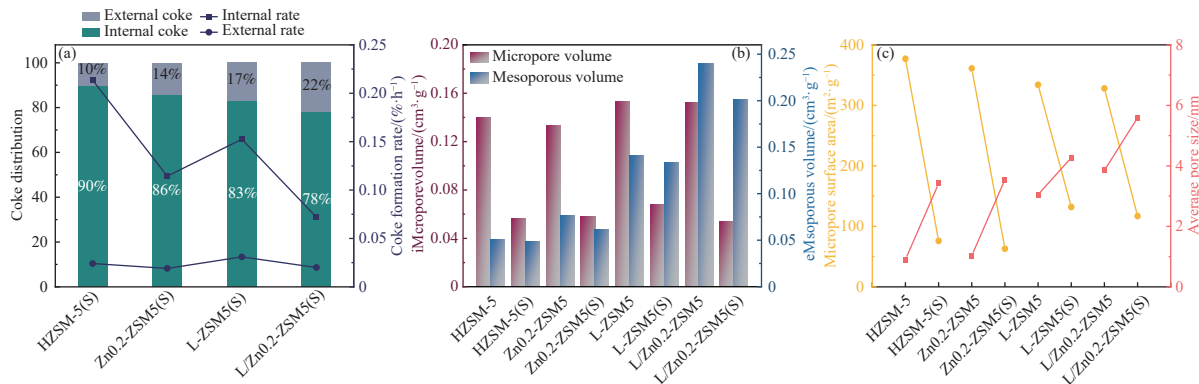


Fig. 12 Evaluation results of catalysts: (a) ratio and rate of internal and external coke accumulation; (b) micro-mesopore pore volume; (c) average micropore specific surface area and pore size

Furthermore, as shown in Figure 12(b), the deactivated catalysts exhibit lower micropore specific surface area and micropore volume than their corresponding fresh catalysts, indicating that coke deposition primarily occurred in the pore mouth region, which blocked the entrances of micropores and hindered the diffusion of product molecules. This situation was further accelerated coke formation within the pores, leading to a rapid reduction in micropore area. Additionally, Figure 12(c) reveals that the average pore sizes of the deactivated catalysts are generally larger than those of their corresponding fresh catalysts. This may be attributed to the deposition of coke at micropore mouths, which blocks some small pores and prevents their detection, resulting in a “pseudo-pore enlargement” phenomenon^[52]. Meanwhile, the accumulation of loose coke creates a “mechanical pore”-like effect, further increasing the average pore size.

3 Conclusion

Compared to single modification with levulinic acid (L-ZSM5) or Zn (Zn0.2-ZSM5), the co-modified HZSM-5 catalyst (L/Zn0.2-ZSM5) introduced an additional mesoporous structure while maintaining a relatively high specific surface area. Furthermore, the proportion of the $[\text{ZnOH}]^+$ active species in L/Zn0.2-ZSM5 increased from 53.09% in Zn0.2-ZSM5 to 61.36%, significantly enhancing its aromatization hydrogen transfer capability. Meanwhile, within the Zn loading range of 0.1%–2.0%, L/Zn0.2-ZSM5 exhibited the highest BTX selectivity (58.75%) and longest catalytic lifetime (128 h).

The co-modification resulted in increases in both mesopore volume and average pore size, along with a decrease in acid amount and acid strength for the L/Zn0.2-ZSM5 catalyst compared to L-ZSM5 and Zn0.2-ZSM5. Consequently, the average coking rate during the MTA reaction was effectively reduced, and the diffusion resistance of coke precursors was reduced. This led to the formation of a loose, hard coke structure with reduced carbon-rich substance content. The proportion of internal coke decreased from 90% in HZSM-5 to 78%, while the catalyst's coke resistance capacity was enhanced.

Declaration of Competing Interest

The authors declare no conflict of interest.

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酸-金属改性 HZSM-5 甲醇芳构化催化剂

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摘 要: 采用乙酰丙酸(LA)和 Zn 对 HZSM-5 进行协同改性, 得到 L/Zn0.2-ZSM5。利用 XRD、N₂ 吸附-脱附、NH₃-TPD、Py-FTIR、Raman、XPS 和 TGA 等对其表征, 研究协同改性对其结构、性质、催化性能及积炭行为的影响。结果表明, L/Zn0.2-ZSM5 的比表面积与 HZSM-5 相当, 孔体积和平均孔径显著大于 HZSM-5 及单一改性样品(L-ZSM5、Zn0.2-ZSM5)。同时, 协同改性显著降低了催化剂的总酸量和酸强度, 并构建了适中的 B/L 酸比。L/Zn0.2-ZSM5 结构及性质的改变, 使其 BTX 催化选择性和催化寿命, 分别达到 58.75% 和 128 h, 均优于单一改性样品及其他 Zn 负载量的样品。L/Zn0.2-ZSM5 的内积炭比例和容炭能力也显著高于未改性和单一改性的样品。这是因为协同改性通过扩孔减弱了积炭前驱体的扩散阻力, 有效抑制了积炭的石墨化进程。同时 LA 增强了 Zn 与载体的相互作用, 促进 Zn 物种的分散, 显著提高了[ZnOH]⁺的比例(达 61.36%)。

关键词: HZSM-5; 乙酰丙酸; Zn; 协同改性; MTA 选择性; 积炭

中图分类号: Q643

文献标识码: A

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