

Influence of the distance between Brønsted acid sites and Mo sites in Mo/HZSM-5 on the mechanism of methane dehydroaromatization performance

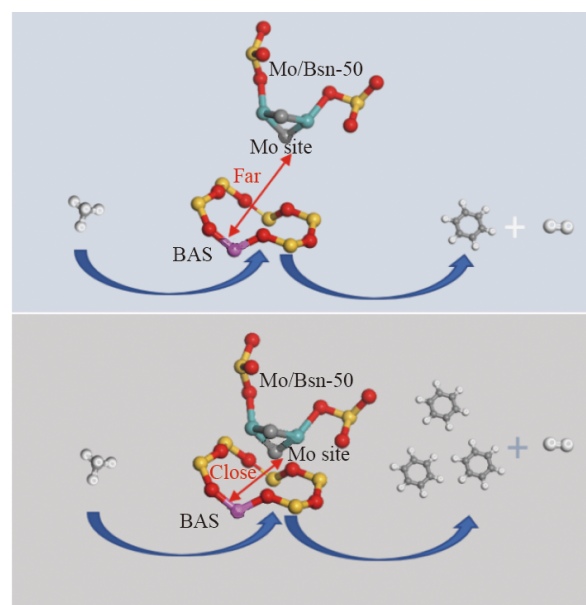
WANG Ce, WEI Lihong*, ZHANG Qinghao, ZHANG Hongxiang, SUN Yuewen

College of Energy and Environment, Shenyang Aerospace University, Shenyang 110100, China

Abstract: Methane dehydroaromatization (MDA) presents a promising carbon-neutral pathway for benzene, toluene, and xylene (BTX) production, alternative to petroleum-derived routes. Elucidating the regulatory mechanisms of Brønsted acid site (BAS) strength on reaction pathways, alongside the spatial proximity effects between BAS and Mo active sites in bifunctional synergy, remains a critical scientific challenge in catalyst design. This study systematically tunes both BAS strength (*via* isomorphous metal substitution) and Mo-BAS spatial proximity in zeolites, integrating MDA catalytic evaluations with density functional theory (DFT) calculations to dissect their individual contributions. Strongly acidic BAS catalysts (compared to moderately acidic Fe/Ga-substituted counterparts) exhibit superior performance, evidenced by enhanced aromatic yields. Conversely, weakly acidic B-substituted zeolites demonstrate optimal mono-/bifunctional synergy, outperforming moderate-acid systems. DFT results reveal that acid strength dictates C–H

activation mechanisms by modulating the energy barriers of rate-determining steps. While Al-zeolites deliver the highest activity, B-substituted systems display unique potential for mechanistic investigations. Spatial proximity analysis indicates that micrometer-scale Mo-BAS distances hinder effective synergy due to exceeding electron interaction and mass transfer limits, whereas nanometer-scale proximity enhances activity (*via* accelerated intermediate transport) and suppresses coke formation. These findings establish a theoretical framework for rationalizing zeolite catalyst optimization through BAS property engineering and spatial control of Mo-BAS cooperation, providing actionable guidelines for designing next-generation MDA catalysts.

Key words: methane dehydroaromatization; Brønsted acid; catalytic mechanism; zeolite



The progressive depletion of crude oil resources, increasing natural gas supply, and sustained growth in chemical demand underscore the significant academic and industrial importance of converting methane (70%–90% of natural gas) into light aromatics^[1]. However, conventional methane conversion technologies, including low-

temperature oxidation to methanol^[2], oxidative coupling to hydrocarbons^[3] and steam reforming to syngas^[4], suffer from critical limitations such as high energy intensity, substantial CO₂ emissions, and multi-step processes. In contrast, non-oxidative methane dehydroaromatization (MDA) over metal-loaded zeolite catalysts has attracted

Received: 2025-09-05; Revised: 2025-10-07

Foundation items: Supported by the Science and Technology Major Project of Liaoning Province (2024JH2, 1025000892), the Fundamental Research Funds for the Universities of Liaoning Province (LJ232410143051), Liaoning Provincial Science and Technology Program 2023JH1/10400006, Shenyang Science and Technology Program (24-213-3-09).

* Corresponding author. Tel: 18040038312, E-mail: weilihong@sau.edu.cn.

DOI: 10.1016/S1872-5813(25)60631-1 CSTR: 32157.14.2097-213X.2025.JFCT.0186

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>)

considerable interest due to its inherent advantages of energy efficiency, reduced carbon footprint, and high aromatic selectivity^[5]. Nevertheless, MDA still faces challenges of inadequate catalyst activity and stability^[6].

Current methane dehydroaromatization (MDA) research predominantly centers on Mo-loaded acidic ZSM-5 zeolites, which are widely regarded as the most promising catalysts for the potential industrial implementation of MDA^[7]. Catalyst deactivation remains a multifaceted challenge, and fundamentally addressing this issue requires elucidating the MDA reaction mechanism. Historically, it was widely accepted that Mo/HZSM-5 operates through a bifunctional mechanism in which CH₄ activation and dehydrogenation occur on Mo sites, while strong BAS catalyze the oligomerization and cyclization of C₂H_x intermediates into benzene and other aromatic products^[8]. Nevertheless, two key challenges persist in understanding the catalytic mechanism: identifying the critical intermediate (where debate centers on acetylene versus ethylene^[9]) and resolving the dichotomy between mono- and bifunctional pathways^[10]. Recent studies confirm that activated molybdenum sites, *via* carbene and methyl radical-mediated pathways, generate both C₂H₂ and C₂H₄, with acetylene identified as the primary precursor to benzene^[11]. At the same time, emerging evidence highlights limitations in the traditional bifunctional theory. For instance, Guo et al.^[12] constructed a Fe@SiO₂ single-atom catalyst (SAC) using atomic layer deposition (ALD) technology. Despite the complete absence of BAS, this catalyst still achieved a methane conversion of 32% and an aromatic selectivity of 47.3%, with no deactivation observed during a 60 h test at 1293 K. Similarly, Gu et al.^[13] introduced 0.5% Na⁺ into Mo/HZSM-5 *via* ion exchange to decrease BAS density; however, the methane conversion was reduced by only 2.1% at 1073 K. Such unexpected results have prompted the community to reassess the essential role of BAS in MDA. This framework overturns classical bifunctionality but raises deeper questions: How do acid strength and optimal Mo-BAS distance correlate? How do they jointly govern hydrocarbon pool species evolution?

These questions can be further contextualized within the broader field of zeolite catalysis. Liu et al.^[14] demonstrated *via* DFT simulations that acid strength serve as an indicator for propylene protonation and C₆ hydrocarbon deprotonation reactivity in methanol-to-olefins (MTO) reactions, highlighting the general applicability of acid strength-reactivity relationships across hydrocarbon conversion processes. Meanwhile, the spatial organization of BAS within catalysts may also exert a critical influence on catalytic performance. Qi et al.^[15] directly probed spatial proximities/interactions between Zn²⁺ ions and BAS at the Angstrom scale using ¹H-⁶⁷Zn double-resonance NMR spectroscopy. Gao et al.^[16] employing ¹H-⁹⁵Mo double-resonance solid-state NMR to uncover the presence of BAS adjacent to Mo species, suggesting potential bifunctional catalytic synergy between these species. Schreiber et al.^[17] and Zhou et al.^[18] combined experimental and

computational studies on framework and extra-framework Ga species. Their studies demonstrated that paired framework Ga and extra-framework Ga sites form the thermodynamically most favorable active sites for the aromatic reaction pathway. This finding provides direct evidence for the synergistic interplay between BAS and Lewis acid sites in zeolite catalysts. Our prior investigations revealed that strongly acidic BAS in close spatial proximity to Mo sites could promote autocatalytic reactions of hydrocarbon pool species, significantly enhancing catalyst activity and directing product conversion toward aromatic compounds^[10]. Nevertheless, quantitatively characterizing the spatial proximity between metal active sites and strong BAS at macroscopic scales remains a substantial challenge.

Therefore, this study employs a multiscale computational-experimental approach to elucidate the regulatory mechanisms of BAS strength on MDA performance. By leveraging isomorphous substitution of Si with different metals (Al, Fe, Ga, B) in the zeolite framework, we systematically modulate BAS acid strength and correlate it with physicochemical properties. Additionally, using silanol nests as anchoring sites, we fabricated 3Mo/Bsn-1 catalysts and precisely controlled the spatial separation between active sites across three scales (millimeter, micrometer, and nanometer) *via* stratified blending, physical mixing, and ball-milling integration. This work not only provides critical guidelines for optimizing BAS acidity in MDA catalysts but also offers mechanistic insights into the synergistic catalysis between Mo sites and strong BAS, advancing the rational design of high-performance MDA catalysts.

1 Methods

1.1 Preparation of catalysts

In this study, metal-substituted MFI-type zeolites were synthesized *via* hydrothermal methods. The synthesis process of the catalyst and the reaction equipment are illustrated in Figure S1. Tetraethyl orthosilicate (TEOS) served as the silicon source, with heteroatom dopants (H₃BO₃, Al(NO₃)₃·9H₂O, Fe(NO₃)₃·9H₂O and Ga(NO₃)₃·xH₂O) introduced to modify the zeolite framework. Tetrapropylammonium hydroxide (TPAOH) was used as the structure-directing agent. The synthesis gel was formulated with a molar ratio of 1 SiO₂:x (H₃BO₃, Al(NO₃)₃·9H₂O, Fe(NO₃)₃·9H₂O, or Ga(NO₃)₃·xH₂O):0.125 TPAOH:8 H₂O, where $x = 0.0200, 0.0125$ and 0.0100 corresponds to Si/*M* ratios of 50, 80 and 100 (*M* = B, Al, Fe, Ga). The components were sequentially mixed in the order of solid, liquid, and template under magnetic stirring at room temperature until a homogeneous transparent solution formed. TEOS was then added dropwise with continuous stirring for 24 h to ensure complete conversion into a white powdery precursor. The mixture was transferred to a stainless-steel autoclave lined with polytetrafluoroethylene

(PTFE) for static crystallization at 175 °C for 7 d. After crystallization, the products were centrifuged and repeatedly washed with deionized water until neutral pH, followed by drying at 60 °C for 12 h under forced-air conditions. Residual organic templates in the pores were removed by calcining the samples in a muffle furnace with a programmed heating rate of 10 °C/min to 550 °C for 8 h. Protonation treatment was conducted using 1 mol/L ammonium chloride (NH₄Cl) solution under stirring at 80 °C for 6 h, followed by secondary calcination at 550 °C for 3 h to obtain the protonated (H-form) zeolites with porous framework structures. Finally, the products were ground, pressed into pellets, and sieved to yield the *M*(B, Al, Fe, Ga)-*X* series (*X* = 50, 80, 100).

The monofunctional zeolite (designated as Bsn-S-1-50) was synthesized *via* a hydrothermal method using tetraethyl orthosilicate (TEOS) as the silicon source, H₃BO₃ as the boron dopant, and tetrapropylammonium hydroxide (TPAOH) as the structure-directing agent. To achieve the target boron loading (Si/B = 50), the synthesis gel was formulated with a molar composition of 1 SiO₂:0.02 H₃BO₃:0.125 TPAOH:8 H₂O. Components were sequentially mixed in the order of solid, liquid, and template agent under mechanical stirring (800 r/min) at room temperature until a homogeneous transparent sol system formed. Continuous stirring for 24 h facilitated TEOS hydrolysis and polycondensation, yielding a white precursor powder. The precursor was transferred to a 50 mL Teflon-lined stainless-steel autoclave for a two-stage crystallization process: initial aging at 100 °C under static conditions for 24 h to promote primary nanoparticle self-assembly, followed by a temperature ramp (7 °C/min) to 175 °C for 7 d to complete MFI topology-directed growth. After crystallization, the product was centrifuged at 10000 r/min for 5 min and repeatedly washed with deionized water until neutral pH to remove unreacted ions and byproducts. The solid was then dried in an oven at 100 °C overnight. Calcination was conducted in a muffle furnace under-static air with a heating rate of 10 °C/min to 550 °C, maintaining the temperature for 8 h to eliminate residual organics. The calcined sample was treated with 1 mol/L NH₄Cl solution at 80 °C for 16 h to extract framework boron atoms and generate silanol nests, followed by re-calcination at 550 °C for 3 h to form the protonated (H-form) structure. This boron-removal cycle was repeated at least twice to ensure complete removal of boron atoms, yielding the final catalyst designated as Bsn-S-1-50.

Molybdenum was loaded onto the ammonium-form zeolite *via* the incipient wetness impregnation method. Specifically, a stoichiometric amount of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) was dissolved in deionized water to fully saturate the pore volume of the support. The resulting solution was then added dropwise to the zeolite under vigorous stirring to ensure uniform distribution of molybdenum precursors. The impregnated sample was dried at 60 °C for 12 h, followed by calcination in static air at 550 °C for 8 h (with a heating rate of

2 °C/min) to optimize Mo species dispersion within the zeolite channels. This thermal treatment promotes the transformation of molybdate precursors into active MoO_x clusters while preserving the structural integrity of the zeolite framework.

This study selected Al-100 (highly acidic HZSM-5, Si/Al=100) and 3Mo/Bsn-50 as model catalyst systems to investigate spatial effects. Composite catalytic systems were fabricated *via* physical mixing of these components to achieve precise spatial segregation between Mo sites and BAS. Three distinct mixing protocols were implemented to control interparticle distances at multiple scales: (1) Stratified mixing (millimeter-scale separation) involved alternating layered deposition of 3Mo/Bsn-50 and Al-100 particles within the reactor tube to enforce macroscopic spatial isolation; (2) Physical mixing (micrometer-scale contact) was achieved through random dry packing of the two components to generate microscale interparticle proximity; (3) Grinding mixing (nanometer-scale integration) employed mortar homogenization of 3Mo/Bsn-50 and Al-100 to induce interfacial fusion and nanoscale contact between moieties.

1.2 Catalyst characterization

The crystallinity of zeolite samples was determined by powder X-ray diffraction (XRD Rigaku Ultima IV). XRD measurements were carried out on a Rigaku Ultima IV benchtop X-ray diffractometer (154.06 pm, 40 kV, 40 mA) with Cu K α radiation at a scan rate of 5(°)/min and a 2 θ range of 5°–60°.

Inductively coupled plasma optical emission spectrometry (ICP-OES) Using Agilent 700 Series ICP-OES, the overall chemical composition of the sample was analyzed by axial plasma observation. Prior to the measurements, samples were dissolved in a mixture of HF (40%), HNO₃ (60%) and H₂O, in a ratio of 1:1:1 by weight.

Surface topographic characterization of the catalyst was conducted using a cold-field emission scanning electron microscope (SEM; Hitachi SU8100). The catalyst powder first underwent planetary ball milling treatment, after which a 50±1 mg sample was uniformly dispersed onto a double-sided conductive carbon tape (thickness: 50 μ m) *via* ultrasonic-assisted dispersion to form a monolayer arrangement. To minimize charging artifacts during SEM imaging, a Au-Pd alloy conductive layer (thickness: 10±2 nm, validated by X-ray reflectometry) was deposited using a magnetron sputtering coater (Emitech K575X, operating at a current of 65 mA) under a high vacuum of 5×10⁻² mbar. Energy-dispersive X-ray spectroscopy (EDS) analysis was performed with an EDAX detection system (USA).

The N₂ adsorption-desorption isotherms were measured using a BELSorp-max volumetric analyzer (JW-BK100) at liquid N₂ temperature (77 K). The Brunauer-Emmet-Teller (BET) equation was used to determine the specific surface

area in the p/p_0 range of 0.05–0.20. The external surface area (S_{ext}) and micropore volume (v_{micro}) of the samples were determined by t -plot analysis. The total pore volume $p/p_0 = 0.95$, and the mesopore volume (v_{meso}) was calculated by subtracting the micropore volume (v_{micro}) from the total pore volume.

The acid properties of the samples were determined by a Bruker Vertex 70 V infrared spectrometer (Py-IR) with pyridine as a probe. The DTGS detector was used in the test, and the number of scans and optical resolution were 100 and 4 cm^{-1} , respectively. The wavelength range is 4000–400 cm^{-1} . 10–15 mg samples are pressed into self-supporting wafers using a custom mold. The sample was then transferred to a vacuum *in situ* cell, heated to 500 °C, and held for 1 h to remove the water and impurities adsorbed on the sample surface. During the cooling process, the spectral backgrounds of 150, 250 and 350 °C were collected. After the mixture was cooled to room temperature, pyridine was introduced and adsorbed for 40 min. Finally, pyridine was desorbed by gradually increasing the temperature, and the spectra at 150, 250 and 350 °C were recorded. The Brønsted acid and Lewis acid of the sample were calculated using the following formula:

$$\text{Lewis acid} = 1.42 \times S_{\text{LR}}^2 / W \quad (1)$$

$$\text{Brønsted acid} = 1.88 \times S_{\text{BR}}^2 / W \quad (2)$$

NH_3 -TPD is performed on a PCA1200 chemical adsorption analyzer equipped with TCD to analyze the acid properties of the samples. About 0.1 g of catalyst was filled in the quartz tube. Before the test, the sample was activated in an Ar stream (30 mL/min) at 300 °C for 2 h and then cooled to 80 °C. For NH_3 -TPD, NH_3 (10% in Ar, 30 mL/min) was introduced on the sample for 60 min to achieve saturated adsorption of NH_3 on the sample. The catalyst was washed with Ar (30 mL/min) at 80 °C for 1 h to remove physically adsorbed NH_3 . Subsequently, the signal changes from 80 to 550 °C were recorded by TPD, and the heating rate was 10 °C/min.

The coke content of the spent catalyst was determined by using a Shimadzu DT-60 H thermogravimetric differential thermal analyzer. Approximately 30 mg of the sample is placed in an alumina crucible. The crucible was heated to 900 °C at a rate of 5 °C in the airflow.

1.3 Catalyst testing

Catalytic methane aromatization was performed in a vertical quartz tube reactor (7 mm i.d. $\times$ 550 mm length) using 0.5 g of catalyst (40–60 mesh). Prior to reaction, the catalyst was pretreated under argon flow with temperature-programmed heating: 10 °C/min to 500 °C followed by 1 °C/min to 700 °C for stabilization. At 700 °C, the feed was switched to 90% CH_4 /10% N_2 at a WHSV of 1.2 h^{-1} . Gaseous products were analyzed online by GC (GC-9070, 5 Å molecular sieve column: 2 m $\times$ 4 mm, TCD) with N_2 as the internal standard. Liquid products were collected in an

n -hexane cold trap, diluted to 50 mL in a volumetric flask, and analyzed offline by GC (GC-9070, capillary column: 30 m $\times$ 0.32 mm $\times$ 0.25 μm , FID). For the stratified-bed catalyst configuration, 0.13 g of quartz wool was employed as the bed support. Two catalyst layers (mass ratio 1:1, 0.25 g each) were separated by a 0.02 g quartz wool spacer to prevent physical intermixing and shifting during operation, while facilitating post-reaction catalyst recovery for characterization.

10% N_2 was added to CH_4 as an internal standard to calculate the conversion of methane (%) in MDA. The calculation process for methane conversion is as follows.

Inlet and outlet flow rates:

$$F^{\text{out}} \times x_{\text{N}_2}^{\text{out}} = F^{\text{in}} \times x_{\text{N}_2}^{\text{in}} \quad (3)$$

where F^{out} represents the outlet flow rate, $x_{\text{N}_2}^{\text{out}}$ outdenotes the detected peak area of nitrogen at the system outlet after the reaction, F^{in} represents the inlet flow rate, $x_{\text{N}_2}^{\text{in}}$ denotes the detected peak area of nitrogen in the feed.

The CH_4 conversion is calculated by the following equation:

$$C_{\text{CH}_4} = \frac{F^{\text{in}} \times x_{\text{CH}_4}^{\text{in}} - F^{\text{out}} \times x_{\text{CH}_4}^{\text{out}}}{F^{\text{in}} \times x_{\text{CH}_4}^{\text{in}}} = \left(1 - \frac{x_{\text{CH}_4}^{\text{out}} \times x_{\text{N}_2}^{\text{in}}}{x_{\text{CH}_4}^{\text{in}} \times x_{\text{N}_2}^{\text{out}}} \right) \times 100\% \quad (4)$$

where C_{CH_4} denotes the methane conversion, $x_{\text{CH}_4}^{\text{in}}$ represents the detected peak area of methane in the feed, and $x_{\text{CH}_4}^{\text{out}}$ represents the detected peak area of methane at the system outlet after the reaction.

Aromatic formation rate:

$$R_i = f_i \times A_i \times n_i \times \frac{F^{\text{out}}}{V_{\text{loop}}} \times \frac{T_{\text{loop}}}{T_o} \times \frac{1}{m_{\text{cat}}} \quad (5)$$

Aromatic selectivity:

$$s_i = \frac{R_i \times m_{\text{cat}} \times 0.0224}{F^{\text{in}} \times x_{\text{CH}_4}^{\text{in}} \times C_{\text{CH}_4}} \times 100\% \quad (6)$$

1.4 Computational details

Spin-polarized DFT calculations were performed using CP2K (v2023.1) with the PBE functional incorporating Grimme's DFT-D3(BJ) dispersion correction under the generalized gradient approximation (GGA)^[19–20]. Electron-ion interactions were described by the Projector Augmented-Wave (PAW) method, validated for accuracy in prior studies. The Gaussian Plane-Wave (GPW) approach with DZVP basis sets and GTH pseudopotentials ensured optimal accuracy-efficiency balance^[21]. Given the large unit cell, Brillouin zone sampling was restricted to the Γ -point. Van der Waals interactions were treated *via* DFT-D3(BJ)^[22]. Convergence tests established CUTOFF = 600 eV and REL_CUTOFF = 55 eV. Post-processing included IGMH analysis, Hirshfeld-partitioned atomic charges, and Independent Gradient Model (IGM) calculations for interatomic interactions *via* Multiwfn 3.8(dev), visualized in VMD^[23–25].

The MFI framework consists of three-dimensionally interconnected 4-, 5- and 6-membered rings, forming

intersecting 10-membered ring (10R) channels: straight channels ($5.3 \text{ \AA} \times 5.6 \text{ \AA}$) along the b -axis and sinusoidal channels ($5.1 \text{ \AA} \times 5.5 \text{ \AA}$) perpendicular to the b -axis^[26]. Cell optimization yielded orthorhombic unit cell parameters ($a = 19.87569 \text{ \AA}$, $b = 19.717607 \text{ \AA}$, $c = 13.142695 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$), which were maintained constant in subsequent calculations. Based on previous literature studies on the isomorphous substitution of Al, B and Ga in the ZSM-5 framework, as well as our team's earlier computational research, (T1, T7) has been identified as one of the most stable among the 12 substitution sites. Among the 12 distinct T-sites within the unit cell, a 6-ring cluster (T1, T7) was chosen for isomorphous substitution of two Si^{4+} ions with Al^{3+} , Fe^{3+} , B^{3+} , or Ga^{3+} to investigate acid site properties and metal anchoring effects. Aligned with the recent experimental and theoretical consensus, dinuclear molybdenum carbide ($\text{Mo}_2\text{C}_2^{2+}$) was selected as the active catalytic species^[27–28].

Transition states were identified using the Dimer method and confirmed *via* vibrational frequency analysis. For elementary steps exhibiting significant temperature-dependent energy contributions, Gibbs free energies at 973 K were calculated using the Shermo^[29], derived from vibrational frequency computations. Reaction activation energies (ΔG) are rigorously defined as the energy difference between the initial state and transition state, whereas reaction Gibbs free energies (ΔG) represent the energy difference between the final and initial states, with negative values correspondingly indicating exothermic processes.

2 Results and discussion

2.1 Catalyst morphology and acidic properties

The XRD characteristic diffraction peaks of MFI-structured zeolites were observed at $2\theta = 7.9^\circ$, 8.7° , 23.0° , 23.8° , 24.4° , 30.78° and 45.02° ^[30]. As illustrated in Figure 1(a) and Figure S2, all synthesized samples exhibited diffraction patterns highly consistent with standard ZSM-5 references, confirming the phase purity of the MFI framework. The sharpness of these diffraction peaks, coupled with their intense intensities, further demonstrated excellent crystallinity without detectable impurity phases.

ICP-OES analysis of isomorphously substituted MFI zeolites ($M = \text{Al, B, Fe, Ga}$) determined Si/ M ratios of Si/B = 113, Si/Fe = 36, Si/Ga = 51 and Si/Al = 75 (Table S1). Moderate discrepancies between experimental and theoretical Si/ M values indicate metal-specific incorporation efficiencies into the zeolite framework^[31]. The highest Si/B ratio results from boron's inferior thermal stability, promoting deborylation under protonic conditions^[32]. Molybdenum loadings were consistent across all samples (2.37%–2.83%) (Table S2).

Through analysis of Figure S3, Table 1 is obtained. Shown in Table 1 are the pore properties of ZSM-5 zeolites (Al-80, B-80, Fe-80, Ga-80), which exhibit Type I behavior characteristic of HZSM-5. BET surface areas and t -plot micropore analyses validated the structural consistency with commercial references.

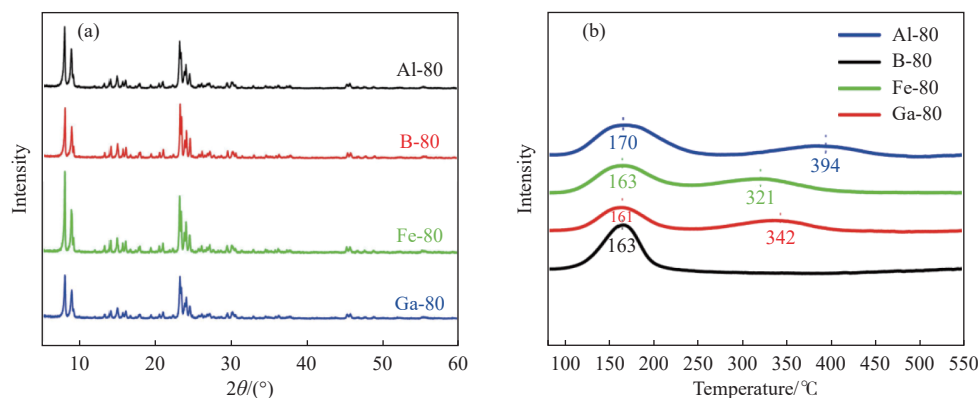


Fig. 1 (a) XRD patterns and (b) NH_3 -TPD profiles of MFI zeolites: M -80 ($M = \text{Al, B, Fe, Ga}$)

Table 1 Sample pore properties of M -80 ($M = \text{Fe, Ga, Al, B}$) and HZSM-5

Catalyst	$S_{\text{BET}}^a / (\text{m}^2 \cdot \text{g}^{-1})$	$S_{\text{micro}}^b / (\text{m}^2 \cdot \text{g}^{-1})$	$S_{\text{ext}}^b / (\text{m}^2 \cdot \text{g}^{-1})$	$v_{\text{total}} / (\text{cm}^3 \cdot \text{g}^{-1})$	$v_{\text{micro}} / (\text{cm}^3 \cdot \text{g}^{-1})$
Al-80	521.67	336.059	185.61	0.364	0.137
B-80	473.55	339.43	134.12	0.241	0.134
Fe-80	470.31	317.78	152.53	0.24	0.12
Ga-80	599.96	412.57	187.39	0.391	0.167
HZSM-5	417.93	340.39	77.54	0.29	0.138

^a: Calculated using the Brunauer-Emmett-Teller equation; ^b: Calculated using the t -plot method.

SEM images (Figure 2) revealed the uniform particle size distributions: Al-substituted ZSM-5 exhibited nanoscale crystallites, whereas other variants displayed micrometer-sized particles, highlighting significant metal-dependent size effects despite identical synthesis conditions. The SEM images of the other zeolites used in this study are provided in Figure S4. EDS elemental mapping (Figure S5) revealed only trace amounts of substituted metals, collectively confirming predominant framework incorporation.

To verify framework incorporation of substituted metals and quantify acid strength, NH_3 -temperature programmed desorption (NH_3 -TPD) (Figure 1(b) and Figure S6) and pyridine infrared spectroscopy (Py-IR) (Table 2) analyses were conducted on isomorphously substituted zeolites. The NH_3 -TPD profiles exhibit distinct acid strength differentiation: B-80 shows significantly weaker BAS acidity with a single desorption peak at 170 °C, whereas Al/Ga/Fe-doped counterparts display dual peaks at 170 °C (weak BAS) and 320–370 °C (strong BAS), attributed to the framework-anchored protons. This discrepancy stems from boron's smaller atomic diameter, which restricts its ability to form tetrahedral Si–O–B bonds with the fourth oxygen atom in SiO_4 tetrahedra, leading to planar trigonal coordination with three oxygen atoms and weaker acid strength^[33–34]. Acid strength follows the order $\text{B} \ll \text{Fe} < \text{Ga} <$

Al, as determined by the temperature of high-temperature desorption peaks (Figure 1(b)). Py-IR analysis quantitatively confirms BAS/Lewis acid site (LAS) densities (Table 2), where exclusive BAS generation from framework-incorporated metals validates successful substitution. Notably, Al-80 exhibits the highest BAS density, while Fe-80 shows exceptional LAS density, indicating the presence of extra-framework Fe species. Catalytic evaluation of Mo-free zeolites (Al-80, B-80, Fe-80 and Ga-80) revealed no MDA activity (Figure S7), demonstrating that extra-framework metal species generated in this study exerted negligible catalytic influence. These results conclusively show that the acid strength of catalysts was precisely tuned through isomorphous metal substitution.

2.2 DFT probes zeolite acid strength and catalytic mechanisms

To further elucidate the influence of heteroatoms on acidity in catalysts, theoretical models of the four types of zeolites were constructed, as shown in Figure S8. We performed first-principles simulations and electronic structure analysis on four types of zeolites.

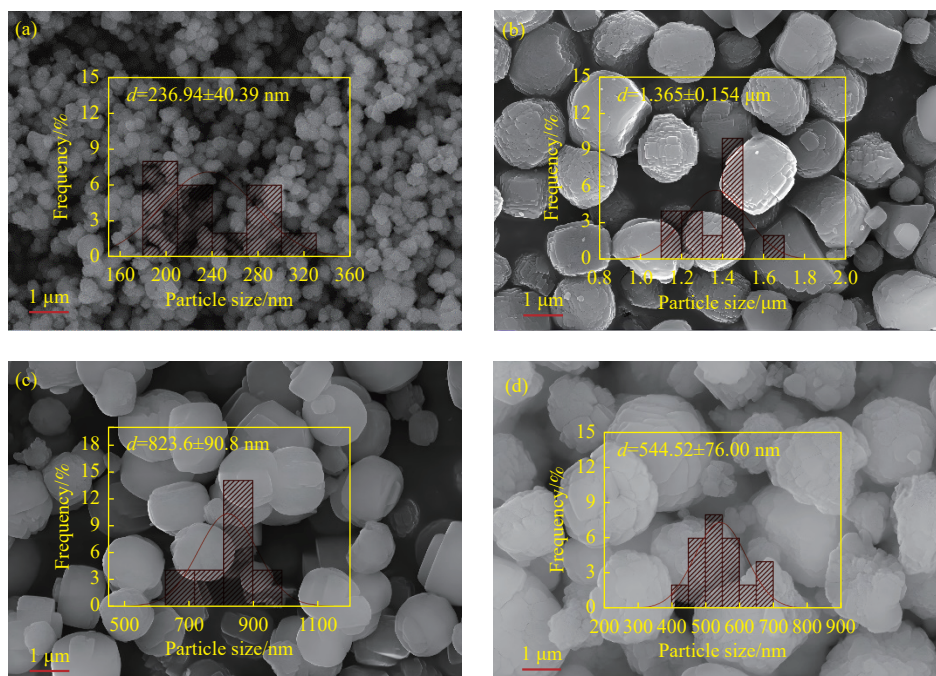


Fig. 2 SEM images of MFI zeolites: (a) Al-80, (b) B-80, (c) Fe-80, (d) Ga-80

Table 2 MFI zeolite Py-IR spectra of catalysts

Catalyst	BAS/($\mu\text{mol} \cdot \text{g}^{-1}$)			LAS/($\mu\text{mol} \cdot \text{g}^{-1}$)		
	150 °C	250 °C	350 °C	150 °C	250 °C	350 °C
Al-80	86	84	78	18	12	0
B-80	34	17	5	6	2	2
Ga-80	29	29	27	10	7	6
Fe-80	44	34	26	67	24	17

As shown in Table 3, the deprotonation energy (DEP, ΔE) was calculated as an indicator of acid strength. A more negative DEP value indicates weaker acidity. Based on the computational results, the acid strength follows this order: B-ZSM-5 << Fe-ZSM-5 < Ga-ZSM-5 < Al-ZSM-5, which is consistent with experimental observations^[35]. Furthermore, the ability of different metal substituents to anchor molybdenum species were compared. Early MDA studies identified Mo_2C detected in spent catalysts as the active phase; however, the true catalytic species are likely dynamically carburizing molybdenum species during the reaction process. Solid state 1D ^{95}Mo NMR and 2D ^1H - ^{95}Mo heteronuclear correlation revealed that molybdenum carbide (MoC_x) species with higher carbide content exhibit enhanced activity for both methane activation and benzene formation^[36]. Based on these experimental observations and theoretical calculations, Mo_2C_2 was selected as the active species due to its thermodynamic stability during the reaction process^[28]. We constructed and optimized structures of Mo_2C_2 anchored at various sites. The binding energies were computed using the expression $\Delta E = E(\text{Mo}_2\text{C}_2/\text{M-ZSM-5}) - E(\text{Mo}_2\text{C}_2) - E(\text{M-ZSM-5})$, revealing distinct anchoring strengths (Table 4): $\text{Mo}_2\text{C}_2/\text{Al-ZSM-5}$ and $\text{Mo}_2\text{C}_2/\text{B-ZSM-5}$ exhibited comparable binding affinities, while $\text{Mo}_2\text{C}_2/\text{Fe-ZSM-5}$ showed the weakest and $\text{Mo}_2\text{C}_2/\text{Ga-ZSM-5}$ the strongest interactions. Structural optimizations yielded consistent Mo–O bond lengths (~ 2.1 Å) across all systems. Quantitative CM5 charge calculations (Figure 3) revealed uniform negative charges on oxygen atoms (-1.6 – -1.783 eV) regardless of the substituted metal, indicating comparable bonding strengths between active sites and the framework in all isomorphously substituted zeolites. Integrated Molecular Graph for Hydrogen Bonding (IGMH) analysis (Figure 4)

visually confirmed strong chemical bond formation between Mo species and anchoring sites, with each Mo center interacting robustly with three framework oxygen atoms.

To determine whether the observed variations in catalytic performance across the four zeolites could be attributed to differences in their active sites, first-principles simulations of the MDA process were conducted. As methane dehydrogenation activation represents the initial and rate-determining step in the MDA reaction pathway, this specific step was simulated^[37–38]. Given comparable Mo-anchoring capabilities across metals (Section 2.2), Al-ZSM-5 exhibiting superior experimental performance—was selected for comprehensive free-energy analysis of BAS anchored Mo_2C_2 species (Figure S9). Methane activation proceeds through dissociative adsorption at dinuclear Mo_2C_2 , forming CH_2^* intermediates and molecular hydrogen. The rate-determining step (RDS) involves concerted C–H bond cleavage of CH_3^* and concurrent C–H bond formation at active sites, with $\Delta G = 1.467$ eV, where hydrogen transfers to adjacent carbon atoms.

Kinetic barriers for this RDS in other metals (Figure 5) follow the order of Al (1.460 eV) < B (1.710 eV) < Ga (1.850 eV) < Fe (2.670 eV), exhibiting a strong inverse correlation with experimental MDA activity (Al > B > Ga > Fe). Lower barriers directly correlate with higher catalytic activity, confirming theoretical predictability. This barrier hierarchy—specifically focused on the mechanistically validated RDS—directly governs overall catalytic activity. Al-ZSM-5's lowest barrier (1.46 eV) aligns with its superior performance. Critically, while metal substitutions minimally affect Mo-anchoring, they significantly modulate RDS barriers through electronic effects that alter Mo– CH_3^* interactions and C–H activation energetics.

Table 3 First-principles calculations of acidity in MFI zeolites

Catalyst	Energy/eV			$\Delta E/\text{eV}$
	E_{ZOH}	$E_{\text{ZO-}}$	$E_{\text{H+}}$	DEP
Al-ZSM-5	−94445.83	−94427.52	−12.62	−5.68
Ga-ZSM-5	−96415.91	−96397.49	−12.62	−5.79
Fe-ZSM-5	−97748.53	−97730.03	−12.62	−5.87
B-ZSM-5	−94465.12	−94446.52	−12.62	−5.97

Table 4 First-principles calculations of energetics and molybdenum species adsorption in MFI zeolites

Catalyst	Energy/eV	$\Delta E_{\text{ads}}/\text{eV}$
Al-ZSM-5	−94373.44	—
B-ZSM-5	−94411.26	—
Fe-ZSM-5	−100978.18	—
Ga-ZSM-5	−98313.37	—
Mo_2C_2	−4011.23	—
$\text{Mo}_2\text{C}_2/\text{Al-ZSM-5}$	−98395.55	−10.88
$\text{Mo}_2\text{C}_2/\text{B-ZSM-5}$	−98433.10	−10.61
$\text{Mo}_2\text{C}_2/\text{Fe-ZSM-5}$	−104998.67	−9.25
$\text{Mo}_2\text{C}_2/\text{Ga-ZSM-5}$	−102335.76	−11.15

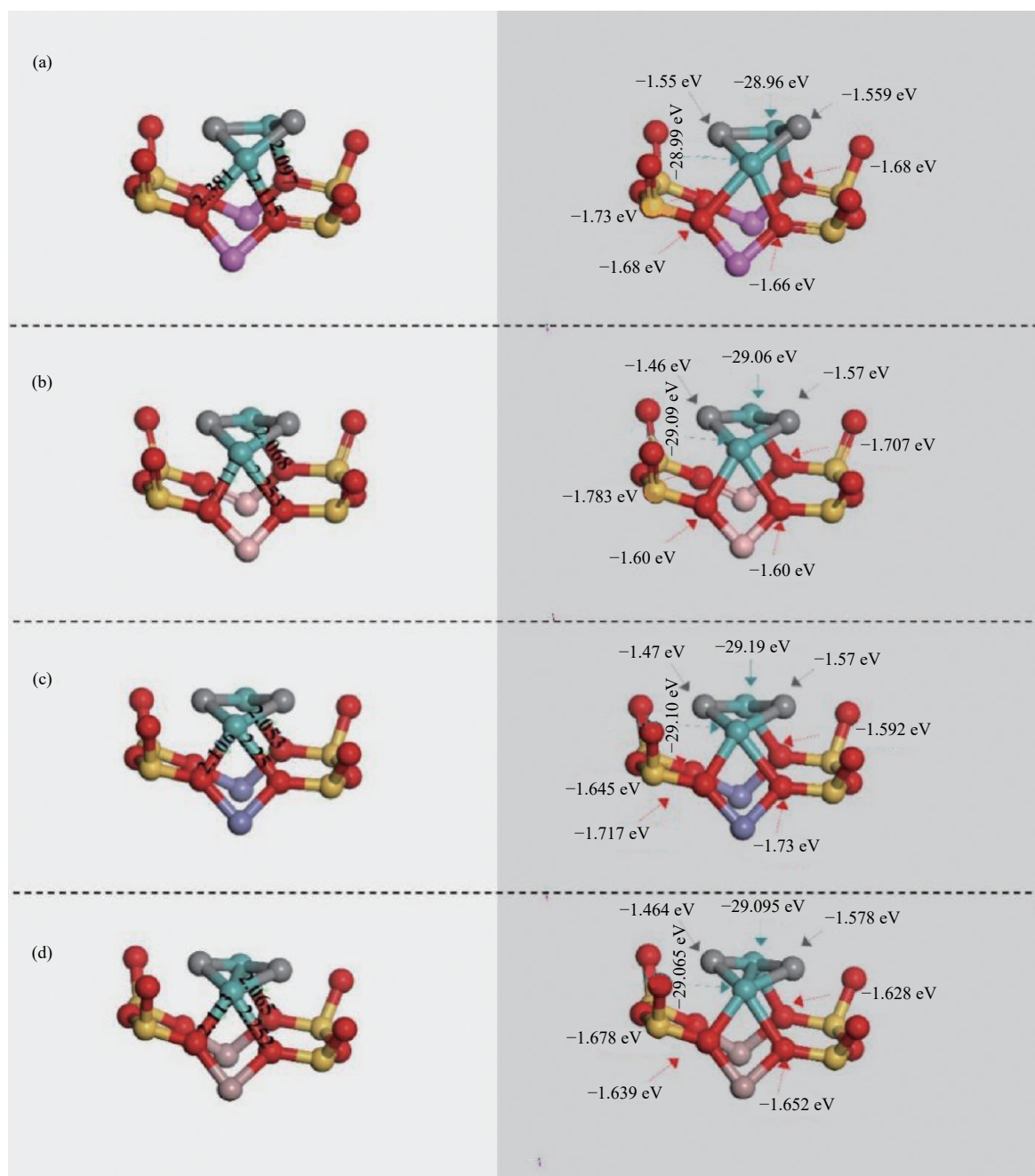


Fig. 3 Bond length and charge analysis of MFI zeolites: (a) $\text{Mo}_2\text{C}_2/\text{Al-ZSM-5}$, (b) $\text{Mo}_2\text{C}_2/\text{B-ZSM-5}$, (c) $\text{Mo}_2\text{C}_2/\text{Fe-ZSM-5}$, (d) $\text{Mo}_2\text{C}_2/\text{Ga-ZSM-5}$

(Gray, red, pink, light pink, purple, brown, yellow and green spheres denote C, O, Al, B, Fe, Ga, Si and Mo atoms, respectively)

2.3 Impact of BAS on catalytic performance in MDA

Catalytic performance was evaluated at 973 K under 13 sccm ($\text{CH}_4:\text{N}_2 = 9:1$) and 1 bar. Triplicate catalytic tests of 3Mo/Al-80 and 3Mo/B-80 (Figure 6(a)) confirmed excellent reproducibility. All catalysts displayed comparable deactivation behaviors (Figure 6(a)), with rapid activity decline within 120 min and stabilization at 3%–4% conversion. Among isomorphously substituted samples, 3Mo/Al-80 exhibited optimal activity, with initial CH_4 conversion of 18.12% that gradually decreased to 5.2%

cumulative conversion over 6 h, yielding 34.12 mg/g BTX (97% benzene). Naphthalene formation was suppressed during synthesis *via* high Si/M ratios. Activity exhibited positive correlation with acidity (Figure 1(b)). However, the catalytic performance of 3Mo/B-80 did not follow the acid strength trend in experiments.

We analyzed the possible reasons for the superior performance of B-isomorphously substituted ZSM-5 and propose the following explanations. Firstly, under high Si/B ratios, prolonged protonation treatment during synthesis induces partial deboronation, generating silanol nests that effectively anchor and disperse Mo species.

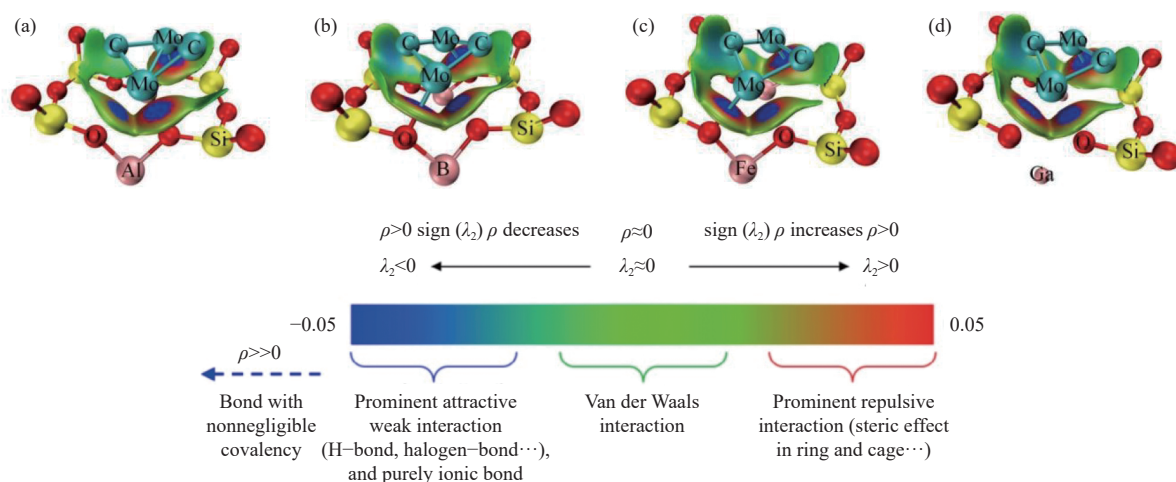
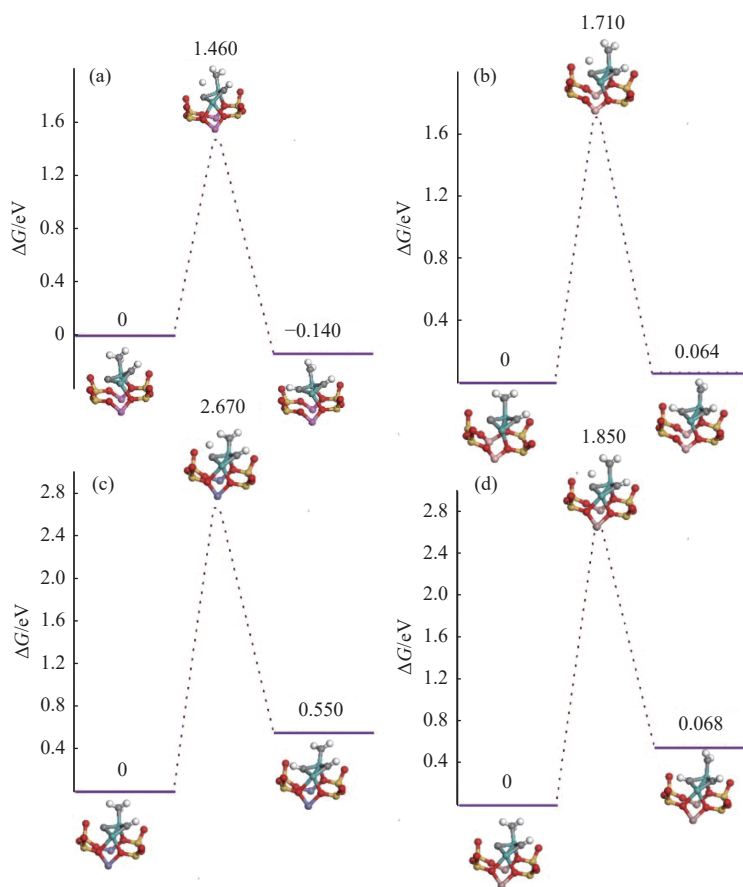


Fig. 4 IGMH analysis of MFI zeolites: (a) $\text{Mo}_2\text{C}_2/\text{Al-ZSM-5}$, (b) $\text{Mo}_2\text{C}_2/\text{B-ZSM-5}$, (c) $\text{Mo}_2\text{C}_2/\text{Fe-ZSM-5}$, (d) $\text{Mo}_2\text{C}_2/\text{Ga-ZSM-5}$



(a) Al-ZSM-5; (b) B-ZSM-5; (c) Fe-HZSM-5; (d) Ga-HZSM-5.

Fig. 5 Thermally corrected free energy barriers for the rate-determining step of methane activation on $\text{Mo}_2\text{C}_2/\text{ZSM-5}$

Secondly, boron incorporation facilitates Mo migration from the catalyst surface into zeolite channels, creating more confined single-atom Mo active sites during MDA reactions^[39]. Additionally, DFT calculations indicate that framework boron exhibits lower acid strength than other heterometals, favoring soft coke formation to prevent pore blockage while maintaining moderate catalytic activity toward hydrocarbon pool species. Due to the harsh reaction conditions of the MDA process and the generation of

numerous intermediates, it is challenging to conduct *in situ* spectroscopic characterization experiments to verify the evolution of species and coke formation. Thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses of spent catalysts after MDA reactions revealed that spent 3Mo/B-80 exhibited the highest weight loss (11.25%), while the other three spent catalysts showed total weight losses between 9.25% and 9.75%. The DTG profiles (Figure 7(b)) displayed two distinct peaks.

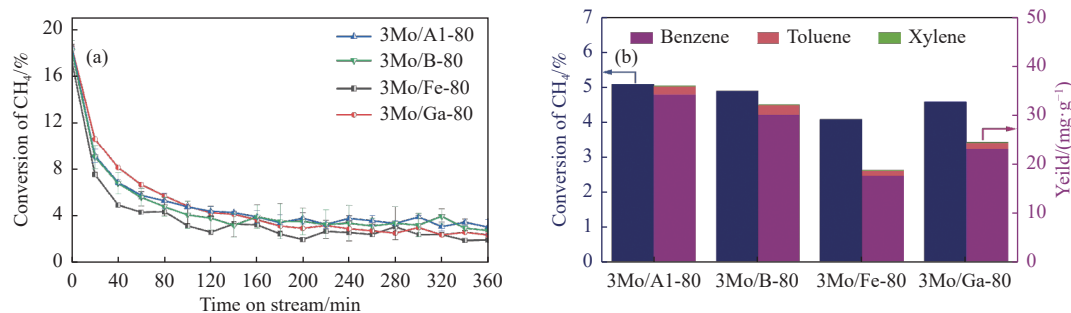


Fig. 6 (a) Time-dependent methane conversion in MDA over 3Mo/M-80 ($M = \text{Fe, Ga, Al, B}$); (b) Cumulative conversion and BTX yields after 6 h MDA reaction for 3Mo/M-80 ($M = \text{Fe, Ga, Al, B}$)

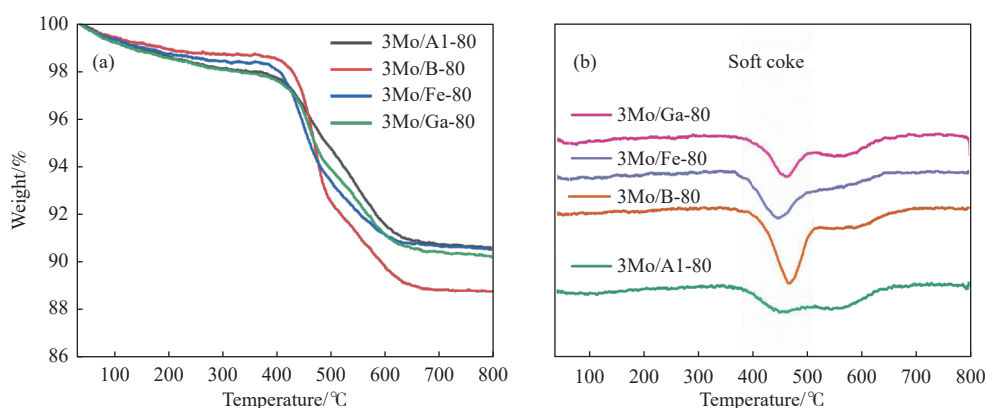


Fig. 7 (a) TG profiles and (b) DTG profiles of spent catalysts: 3Mo/B-80, 3Mo/Al-80, 3Mo/Ga-80, 3Mo/Fe-80

The low-temperature peak ($\sim 470^\circ\text{C}$) corresponds to the combustion of soft coke, which primarily forms during the initial reaction stage through alkylation or oligomerization of aromatics, generating linear alkylbenzenes and condensed polycyclic aromatic precursors. This soft coke blocks pores without damaging the framework structure and reduces active site density by covering Brønsted acid sites. An increased proportion of soft coke typically indicates higher catalytic activity. With decreasing acidity, the low-temperature peak intensified, signifying a greater proportion of soft coke in the total coke. The high temperature peak ($\sim 550^\circ\text{C}$) corresponds to hard coke combustion.

Hard coke originates from deep dehydrogenation and condensation at elevated temperatures, where soft coke undergoes progressive dehydrogenation at acid sites, forming highly condensed polycyclic aromatics that stack *via* π - π interaction, generating graphitic carbon layers within the pores. Hard coke is more graphitized than soft coke and negatively impacts catalyst coking behavior and reaction sustainability^[40–42]. The soft coke content followed the order: $\text{B} > \text{Fe} > \text{Ga}$, with the boron-containing catalyst exhibiting the highest soft coke content. In the low-temperature TG region, the spent catalyst displayed negligible weight loss, indicating that its micropores were not severely blocked. At 400 – 600°C , the catalyst underwent substantial weight loss, suggesting a high level of carbon deposition and severe coverage of micropore entrances and external surfaces—with the carbon primarily in the form of amorphous carbon. Moreover, above 600°C , the catalyst's weight remained stable, indicating no obvious

damage to its framework structure. Since hydrocarbon pool (HCP) species positively correlate with soft coke confined within the zeolite, this indicates that 3Mo/B-80 generated more HCP species during the reaction. Concurrently, the weaker Brønsted acidity of boron promoted the monofunctional mechanism, thereby enhancing BTX yield.

The influence of boron content on catalytic performance was further examined. As illustrated in Figure 8, decreasing the Si/B ratio resulted in increased cumulative methane conversion and aromatic yields. This trend stems from two synergistic mechanisms: (1) Increased BAS density at lower Si/B ratios accelerates olefin-to-aromatics conversion; (2) Enhanced spatial proximity between Mo active sites and BAS shortens diffusion pathways for Mo-generated olefins to BAS, facilitating accelerated cyclization.

To investigate the effect of framework boron removal in boron B-isomorphously substituted ZSM-5 zeolite on its catalytic performance for MDA, this study leveraged insights from prior research showing that hydrothermal dealumination decreases BAS density in ZSM-5, thereby enhancing the stability of intermediate aromatic compound^[43]. Therefore, tailored protonation (hydrothermal treatment) of the HB-80 precursor was conducted for varying durations ($x = 4, 8, 16$ h) to achieve controlled deboronation. A series of molybdenum-loaded catalysts, denoted 3Mo/B-80- x were subsequently prepared using these modified supports. Prolonged hydrothermal treatment increased the number of silanol nests while gradually decreasing BAS density. MDA performance results for this

catalyst series are shown in Figure 9. Catalytic testing revealed that the non-hydrothermally treated 3Mo/B-80 catalyst, containing residual framework boron, exhibited optimal MDA performance with a BTX yield of 31.5 mg/g. Notably, as deboronation time increased, methane conversion remained largely unchanged, but BTX yield decreased significantly and stabilized after 8 h of treatment, indicating complete framework boron removal at this stage. This performance trend correlates directly with mechanistic shifts: while BAS-free catalysts (relying solely on silanol nests to anchor Mo species) can catalyze MDA *via* the HCP mechanism, their activity is substantially lower. In contrast,

the 3Mo/B-80 system utilizes residual boron-derived weak BAS to activate a bifunctional pathway. We propose that the superior performance of 3Mo/B-80 stems from the synergistic operation of dual mechanisms: (i) a monofunctional pathway dominated by Mo sites anchored at silanol nests (responsible for methane activation), and (ii) a bifunctional pathway involving weak BAS (promoting aromatization). Critically, this synergy enables 3Mo/B-80 to outperform the conventional 3Mo/Al-80 system (which operates exclusively *via* a bifunctional mechanism relying on stronger BAS), highlighting the pivotal role of weak BAS in optimizing dual-pathway cooperativity.

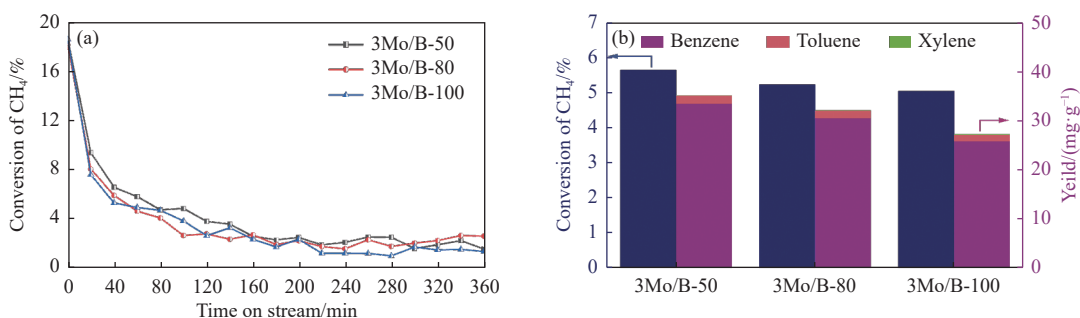


Fig. 8 (a) Time-dependent methane conversion in MDA over 3Mo/B- X ($X = 50, 80, 100$); (b) Cumulative conversion and aromatic yields after 6 h MDA for 3Mo/B- X ($X = 50, 80, 100$)

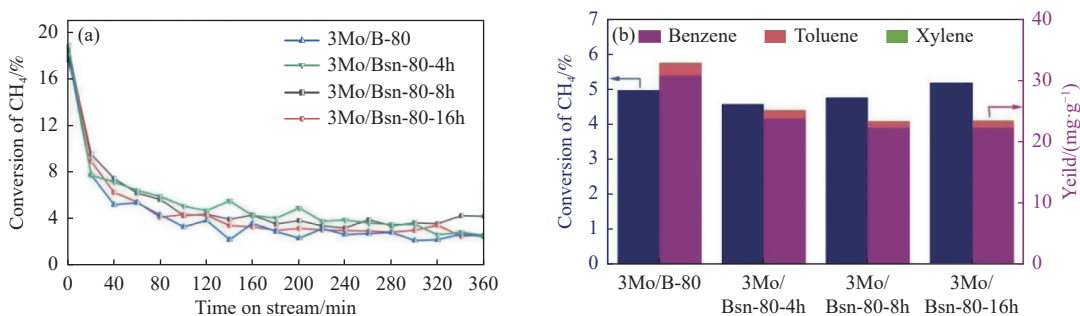


Fig. 9 (a) Time-dependent methane conversion in MDA over 3Mo/Bsn-80- x h ($x = 4, 8, 16$); (b) Cumulative conversion and aromatic yields after 6 h MDA for 3Mo/Bsn-80- x h ($x = 4, 8, 16$)

2.4 Synergistic effects of BAS-Mo spatial proximity on MDA performance

Building on reported mechanisms where spatial proximity between BAS and Mo species promotes autocatalytic reactions of hydrocarbon pool intermediates, thereby enhancing aromatic formation rates and catalyst activity, this study systematically modulates spatial separation scales to probe mono-/bifunctional synergy. Since it remains challenging to quantitatively determine the spatial distance between spatially separated metal ions and Brønsted acid sites (BAS) even with HAADF-STEM and double-resonance solid-state NMR techniques. Physical mixtures were constructed using a monofunctional catalyst (3Mo/Bsn-50, BAS-free) and an acidic zeolite (Al-100). Following the model proposed by Xiao et al.^[44], millimeter-scale, micrometer-scale, and nanometer-scale spatially

separated systems were constructed using three distinct methods: layered mixing, physical mixing, and grinding mixing. Notably, catalyst particles with a uniform size distribution (200–300 nm) were employed and the spatial separation distance was maintained at approximately the sum of the radii of particles from the two phases, ensuring precise control over the spatial scale across the different mixing techniques. Catalytic performance evaluations (Figure 10) demonstrated that physically mixed system exhibited only marginal improvements of 9.5% in methane conversion and 15% in BTX yield compared to the layered configuration. In contrast, the ball-milled mixture demonstrated optimal performance: methane conversion stabilizing at 6% after 2 h and a total BTX yield of 26.3 mg/g. Analyzing the increased spatial proximity between Mo₂C species and BAS (spanning millimeter-scale, microscale, to nanoscale), we attribute the significantly enhanced activity primarily to

intensified bifunctional synergy at reduced Mo-BAS distances, based on our prior mechanistic studies^[12]. This trend establishes a clear monotonic relationship between spatial proximity and bifunctional cooperativity. Furthermore, nanoscale reduction of the Mo-BAS distance effectively shortens the diffusion path for intermediates, accelerating aromatization reaction kinetics.

This result highlights that, although spatial proximity is

crucial for aromatization, precise molecular-scale engineering of metal-acid center configurations faces two major challenges: (1) Controlled modification of Mo anchoring sites within zeolite channels, and (2) Atomic-level spatial coordination design between BAS and metal active centers. These findings provide a theoretical framework for the development of advanced bifunctional catalysts with tailored active center spatial distributions.

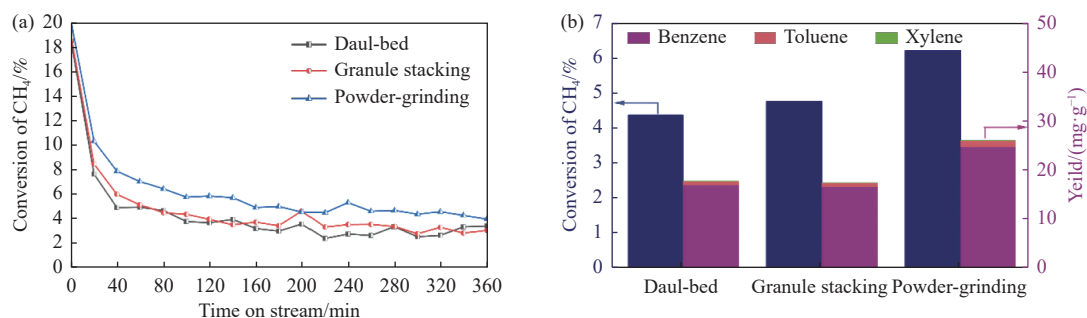


Fig. 10 (a) Time-dependent methane conversion in MDA for 3Mo/Bsn-50 and Al-100 different mixing methods; (b) Cumulative conversion and aromatic yields after 6 h MDA for 3Mo/B-50 and Al-100 under different mixing methods

3 Conclusions

This study adopts a multiscale approach that integrates systematic experiments with theoretical calculations to elucidate the synergistic regulation of catalytic performance in methane dehydroaromatization (MDA) by zeolitic BAS strength and the spatial distribution of active centers. The key conclusions are as follows:

Methane conversion scales with BAS strength in *M*-80 (Al > Ga > Fe). The difference is that B-80 achieves exceptional MDA performance through synergetic catalysis: deboronation-generated silanol nests anchor Mo for monofunctional steps, while residual framework boron provides weak BAS activity.

Atomic-scale Mo-BAS spatial proximity significantly modulates hydrocarbon pool activity in MDA. Ball milling achieves optimal nanoscale spacing, outperforming millimeter/micrometer mixtures. This enhanced interfacial synergy increases methane conversion by 33% and BTX yield by 31%, establishing spatial confinement as the performance-determining factor.

DFT calculations confirm deprotonation energy (DPE) correlates with experimental acid strength. For strong-acid Al-ZSM-5 (DPE = −5.68 eV), C–H bond dissociation barrier ($\Delta G = 1.467$ eV) is significantly lowered. IGMH analysis reveals mixed ionic-covalent character of Mo–O bonds, stabilized by charge compensation and geometric compatibility. First-principles simulations show metal substituents modulate active centers' electronic structure—not merely serving as anchors—thereby governing CH₃ C–H cleavage barriers and overall activity.

The core contribution of this study lies in establishing a multi-scale catalytic mechanism framework of acid strength–spatial confinement–electronic modulation. This provides a critical theoretical foundation for the rational design of high-performance MDA catalysts. Future research

can expand into novel metal-doped systems, optimizing the Mo-BAS interaction through synergistic effects to ultimately advance the industrial application of MDA catalysts.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] ZAMAN S, SMITH K J. A review of molybdenum catalysts for synthesis gas conversion to alcohols: Catalysts, mechanisms and kinetics[J]. Catal Rev, 2012, 54(1): 41–132.
- [2] KIANI D, SOURAV S, BALTRUSAITIS J, et al. Oxidative coupling of methane (OCM) by SiO₂-supported tungsten oxide catalysts promoted with Mn and Na[J]. ACS Catal, 2019, 9(7): 5912–5928.
- [3] KIANI D, SOURAV S, TAIFAN W, et al. Existence and properties of isolated catalytic sites on the surface of β -cristobalite-supported, doped tungsten oxide catalysts (WO_x/ β -SiO₂, Na-WO_x/ β -SiO₂, Mn-WO_x/ β -SiO₂) for oxidative coupling of methane (OCM): A combined periodic DFT and experimental study[J]. ACS Catal, 2020, 10(8): 4580–4592.
- [4] LI P, SAKURAGI K, MAKINO H. Extraction techniques in sustainable biofuel production: A concise review[J]. Fuel Process Technol, 2019, 193: 295–303.
- [5] JUNG W, LIM Y H, KIM H, et al. Kinetic modeling of methane dehydroaromatization over Mo/ZSM-5 catalysts[J]. Chem Eng J, 2024, 496: 153616.
- [6] SPIVEY J J, HUTCHINGS G. Catalytic aromatization of methane[J]. Chem Soc Rev, 2014, 43(3): 792–803.
- [7] WANG L, TAO L, XIE M, et al. Dehydrogenation and aromatization of methane under non-oxidizing conditions[J]. Catal Lett, 1993, 21(1): 35–41.

- [8] KUMAR A, SONG K, LIU L, et al. Absorptive hydrogen scavenging for enhanced aromatics yield during non-oxidative methane dehydroaromatization on Mo/H-ZSM-5 catalysts[J]. *Angew Chem Int Ed*, 2018, 57(47): 15577–15582.
- [9] ÇAĞLAYAN M, LUCINI PAIONI A, ABOU-HAMAD E, et al. Initial carbon-carbon bond formation during the early stages of methane dehydroaromatization[J]. *Angew Chem Int Ed*, 2020, 59(38): 16741–16746.
- [10] ZHANG H, WEI L, SUN Y, et al. Brønsted acid site catalytic role in methane dehydroaromatization over Mo/HZSM-5[J]. *ACS Catal*, 2024, 14(15): 11591–11603.
- [11] PENG L, ZHANG H, XIAO T, et al. Elucidating the formation mechanism and catalytic role of C1 intermediates in the initial stages of methane dehydroaromatization over Mo/HZSM-5[J]. *ACS Catal*, 2025, 15: 11123–11133.
- [12] GUO X, FANG G, LI G, et al. Direct, nonoxidative conversion of methane to ethylene, aromatics, and hydrogen[J]. *Science*, 2014, 344(6184): 616–619.
- [13] GU Y, CHEN P, YAN H, et al. Coking mechanism of Mo/ZSM-5 catalyst in methane dehydroaromatization[J]. *Appl Catal A: Gen*, 2021, 613: 118019.
- [14] LIU P, HAN J, LING L, et al. Correlation of Brønsted acid strengths and species substituted Si in ZSM-5 and their effects on propylene polymerization in MTA reaction[J]. *Microporous Mesoporous Mater*, 2023, 347: 112346.
- [15] QI G, WANG Q, XU J, et al. Synergic effect of active sites in zinc-modified ZSM-5 zeolites as revealed by high-field solid-state NMR spectroscopy[J]. *Angew Chem Int Ed*, 2016, 128(51): 16058–16062.
- [16] GAO W, QI G, WANG Q, et al. Dual active sites on molybdenum/ZSM-5 catalyst for methane dehydroaromatization: Insights from solid-state NMR spectroscopy[J]. *Angew Chem Int Ed*, 2021, 133(19): 10804–10810.
- [17] SCHREIBER M W, PLAISANCE C P, BAUMGARTL M, et al. Lewis–Brønsted acid pairs in Ga/H-ZSM-5 to catalyze dehydrogenation of light alkanes[J]. *J Am Chem Soc*, 2018, 140(14): 4849–4859.
- [18] ZHOU Y, THIRUMALAI H, SMITH S K, et al. Ethylene dehydroaromatization over Ga-ZSM-5 catalysts: Nature and role of gallium speciation[J]. *Angew Chem Int Ed*, 2020, 59(44): 19592–19601.
- [19] KÜHNE T D, IANNUZZI M, DEL BEN M, et al. CP2K: An electronic structure and molecular dynamics software package-Quickstep: Efficient and accurate electronic structure calculations[J]. *J Chem Phys*, 2020, 152(19), No. 194103.
- [20] STANCIAKOVA K, ENSING B, GOLTL F, et al. Cooperative role of water molecules during the initial stage of water-induced zeolite dealumination[J]. *ACS Catal*, 2019, 9(6): 5119–5135.
- [21] VANDEVONDELE J, KRACK M, MOHAMED F, et al. Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach[J]. *Comput Phys Commun*, 2005, 167(2): 103–128.
- [22] GRIMME S, EHRLICH S, GOERIGK L. Effect of the damping function in dispersion corrected density functional theory[J]. *J Comput Chem*, 2011, 32(7): 1456–1465.
- [23] LU T, CHEN F. Multiwfn: A multifunctional wavefunction analyzer[J]. *J Comput Chem*, 2012, 33(5): 580–592.
- [24] LU T, CHEN Q. Independent gradient model based on Hirshfeld partition: A new method for visual study of interactions in chemical systems[J]. *J Comput Chem*, 2022, 43(8): 539–555.
- [25] HUMPHREY W, DALKE A, SCHULTEN K. VMD: Visual molecular dynamics[J]. *J Mol Graph*, 1996, 14(1): 33–38.
- [26] KNOTT B C, NIMLOS C T, ROBICHAUD D J, et al. Consideration of the aluminum distribution in zeolites in theoretical and experimental catalysis research[J]. *ACS Catal*, 2018, 8(2): 770–784.
- [27] VOLLMER I, KOSINOV N, SZÉCSÉNYI Á, et al. A site-sensitive quasi-in situ strategy to characterize Mo/HZSM-5 during activation[J]. *J Catal*, 2019, 370: 321–331.
- [28] LI G, VOLLMER I, LIU C, et al. Structure and reactivity of the Mo/ZSM-5 dehydroaromatization catalyst: An operando computational study[J]. *ACS Catal*, 2019, 9(9): 8731–8737.
- [29] LU T, CHEN Q. Shermo: A general code for calculating molecular thermochemistry properties[J]. *Comput Theor Chem*, 2021, 1200: 113249.
- [30] LIM Y H, KIM H, LEE H, et al. Application of HCl treatment to tailor the Ga species and propane aromatization performance of various Ga incorporated MFI catalysts[J]. *J Catal*, 2023, 422: 24–35.
- [31] LIU Y, BOLSHAKOV A, COZA M, et al. Isomorphously substituted [Fe, Al] ZSM-5 catalysts for methane dehydroaromatization[J]. *ACS Catal*, 2023, 13(12): 8128–8138.
- [32] LI C, VIDAL-MOYA A, MIGUEL P J, et al. Selective introduction of acid sites in different confined positions in ZSM-5 and its catalytic implications[J]. *ACS Catal*, 2018, 8(8): 7688–7697.
- [33] CHEN P, WANG X, YU R, et al. Enhancing metal dispersion over an Mo/ZSM-5 catalyst for methane dehydroaromatization[J]. *Inorg Chem Front*, 2022, 9(18): 4642–4650.
- [34] HE P, WANG A, MENG S, et al. Impact of Al sites on the methane co-aromatization with alkanes over Zn/HZSM-5[J]. *Catal Today*, 2019, 323: 94–104.
- [35] YUAN S P, WANG J G, LI Y W, et al. Brønsted acidity of isomorphously substituted ZSM-5 by B, Al, Ga, and Fe. Density functional investigations[J]. *Phys Chem A*, 2002, 106(35): 8167–8172.
- [36] GAO W, WANG Q, QI G, et al. Active ensembles in methane dehydroaromatization over molybdenum/ZSM-5 zeolite identified by 2D 1H–95Mo magic angle spinning nuclear magnetic resonance correlation spectroscopy[J]. *Angew Chem Int Ed*, 2023, 62(31): e202306133.
- [37] HUANG X, EGGART D, QIN G, et al. Methyl radical chemistry in non-oxidative methane activation over metal single sites[J]. *Nat Commun*, 2023, 14(1): 5716.
- [38] ZHANG H, WEI L, SUN Y, ET AL. Transformation of metal species and catalytic reaction mechanism of metal modified ZSM-5 in alkane aromatization[J]. *Fuel Process Technol*, 2023, 245: 107739.
- [39] HUANG X, WANG L, GAO L, et al. Boron assists molybdenum to be confining single atoms for methane

- dehydroaromatization[J]. Fuel, 2025, 384: 134040.
- [40] TEMPELMAN C H L, HENSEN E J M. On the deactivation of Mo/HZSM-5 in the methane dehydroaromatization reaction[J]. Appl Catal B: Environ, 2015, 176: 731–739.
- [41] KOSINOV N, USLAMIN E A, COUMANS F J A G, et al. Structure and evolution of confined carbon species during methane dehydroaromatization over Mo/ZSM-5[J]. ACS Catal, 2018, 8(9): 8459–8467.
- [42] KOSINOV N, USLAMIN E A, MENG L, et al. Reversible nature of coke formation on Mo/ZSM-5 methane dehydroaromatization catalysts[J]. Angew Chem Int Ed, 2019, 131(21): 7142–7146.
- [43] SIM T J, SHIM J, LEE G, et al. Tailored chemical modification of ZSM-5 zeolite supports for Mo-based catalysts optimized for methane dehydroaromatization: Hydrothermal dealumination was key to improving the selectivity of desired aromatic compounds[J]. Catal Today, 2024, 425: 114357.
- [44] XIAO P, WANG Y, WANG L, et al. Understanding the effect of spatially separated Cu and acid sites in zeolite catalysts on oxidation of methane[J]. Nat Commun, 2024, 15(1): 2718.

Brønsted 酸位与钼活性位点间距对 Mo/HZSM-5 催化剂甲烷脱氢芳构化反应机制的影响

王 策, 魏砾宏*, 张清昊, 张宏祥, 孙悦文

(沈阳航空航天大学 能源与环境学院 辽宁 沈阳 110100)

摘 要: 甲烷脱氢芳构化(MDA)作为一种潜在的碳中和技术路径,为苯、甲苯和二甲苯(BTX)的生产提供了石油路线之外的替代方案。阐明布朗斯特酸位(BAS)强度对反应路径的调控机制,以及双功能协同中 BAS 与钼活性位点的空间邻近效应,仍是催化剂设计领域的关键科学难题。本研究通过同晶金属取代调控分子筛的酸强度,并系统调节 Mo-BAS 空间距离,结合 MDA 催化性能评价与密度泛函理论(DFT)计算,解析了两者的独立作用机制。强酸性 BAS 催化剂(相较于中酸性的铁/镓取代体系)表现出更优异的芳烃收率;而弱酸性硼取代分子筛则展现出最佳的单/双功能协同效应,性能超越中酸体系。DFT 模拟表明,酸强度通过调控决速步能垒主导 C-H 活化机制: 铝取代分子筛具有最高活性,硼取代体系则展现出独特的机理研究价值。空间邻近性分析揭示,微米级 Mo-BAS 距离因超出电子相互作用与传质极限而阻碍协同效能,纳米级邻近则通过加速中间体传输提升反应活性,并有效抑制积炭形成。这些发现建立了通过 BAS 性质调控与 Mo-BAS 空间协作优化分子筛催化剂的理论框架,为设计新一代 MDA 催化剂提供了可操作的指导原则。

关键词: 甲烷脱氢芳构化; 布朗斯特酸; 催化机理; 沸石

中图分类号: O643.36

文献标识码: A

作者简介:



王策(2000), 硕士, 研究方向为甲烷脱氢芳构化, whw13354431279@163.com。