

The influence of acidity on the performance of propylene oligomerization over HZSM-5 catalysts

LI Wei^{1,2}, WANG Hui^{2,3,*}, ZHANG Jinzhi^{2,3}, XU Xi^{2,3}, GUO Xingcui^{2,3}, JIAO Tiantian^{1,*}, WU Jinhu^{2,3}

¹ School of Chemistry and Bioengineering, Shandong University of Science and Technology, Qingdao 266590, China;

² Qingdao Institute of Bioenergy and Process, Chinese Academy of Sciences, Qingdao 266101, China;

³ Shandong Energy Institute, Qingdao 266101, China

Abstract: HZSM-5 zeolite catalysts with different Si/Al ratios were synthesized by the hydrothermal method. The catalytic performance of these HZSM-5 zeolites with varying Si/Al ratios in propylene oligomerization was investigated. The structure, composition, and acidity of the catalysts were analyzed using XRD, SEM, N₂ physisorption-desorption, NH₃-TPD and so on. A comparative study was conducted on the catalytic performance in propylene oligomerization over HZSM-5 with different Si/Al ratios (30, 50, 90 and 120). The results indicate that as the Si/Al ratio increases, the catalyst acidity decreases, and the temperature for maximum liquid oil yield from propylene oligomerization shifts to higher temperatures, specifically 360, 380, 440 and 460 °C, respectively. This study focuses on elucidating the relationship between the acidity of HZSM-5 zeolites with different Si/Al ratios and the product distribution as well as the reaction pathways in propylene oligomerization. The research indicates that HZSM-5 zeolites with lower Si/Al ratios possess higher acid site density, which favors the occurrence of propylene oligomerization, with the reaction products primarily consisting of olefins. In contrast, HZSM-5 catalysts with higher Si/Al ratios are more conducive to further reactions of propylene and the primary olefinic products from oligomerization, such as cyclization and aromatization and hydrogen transfer. Consequently, the product distribution is broader, encompassing olefins, cycloalkanes, aromatics, and alkanes.

Key words: HZSM-5; propene; oligomerization; acidity



As a cornerstone of the modern chemical industry, propylene's production capacity and supply-demand dynamics are central to the global petrochemical industry. In recent years, driven by the development of coal/methanol-to-olefins (MTO) technology and the large-scale commissioning of propane dehydrogenation (PDH) routes, propylene production capacity has surged^[1]. Currently, domestic propylene has entered a stage of overcapacity; therefore, identifying high-value upgrading pathways for propylene products holds significant practical importance.

Propylene oligomerization is a crucial reaction for converting propylene into high-value-added products and improving resource utilization. Against the backdrop of the

carbon neutrality strategies, propylene oligomerization serves as a vital bridge for renewable energy utilization^[2-5]. It can be employed to produce high-quality green fuels, such as environmentally friendly gasoline (C₅–C₁₂), sustainable aviation fuel (SAF C₈–C₁₆) and diesel fuel (C₁₁–C₂₄)^[6-13], possessing irreplaceable strategic significance for meeting the market demand for green fuels.

While some commercial light olefin oligomerization processes utilize homogeneous catalysts, heterogeneous catalysts are increasingly preferred under green chemistry principles due to their high efficiency, ease of recovery, and potential for reuse. Solid acid catalysts, particularly zeolite molecular sieves, have become the most favored

Received: 2025-12-29; Revised: 2026-01-28

Foundation items: Supported by National Natural Science Foundation of China (22308366) and Shandong Provincial Key Research and Development Program, China (2025CXPT181).

* Corresponding author. Tel: 0532-80662761, Fax: 0532-80662761, E-mail: wang_hui@qibebt.ac.cn, jiaotiantian1988@163.com.

DOI: 10.1016/S1872-5813(26)60699-8 CSTR: 32157.14.2097-213X.2026.JFCT.0058 Associated Data DOI: 10.57760/sciencedb.j00124.00441

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>)

heterogeneous catalysts for light olefin oligomerization due to their cost-effectiveness and excellent shape selectivity^[6,14–18]. The catalysis of propylene oligomerization by HZSM-5 (MFI topology) molecular sieves is of great significance for upgrading light olefins into fuel-range hydrocarbons.

Previous studies indicate that the physicochemical properties of molecular sieve catalysts, such as pore structure and acidity, significantly influence the rate and selectivity of the propylene oligomerization reaction, as well as the distribution of product composition^[19–23]. Mlinar et al.^[24] observed that under fixed space velocity conditions (4 s^{-1}), the propylene conversion (25 kPa C_3H_6 , 513K) over commercial H-MFI samples (Si/Al ratio 13–140) decreased systematically as aluminum content increased. This was attributed to reduction in the trimerization rate caused by steric crowding, essentially, a higher density of H^+ sites increases adsorbate density, hindering the reaction. Therefore, both the density and distribution of acid sites, as well as the zeolite topology, have a substantial impact on the propylene oligomerization reaction.

Bickel et al.^[22] investigated the effects of acid site density and crystal size of HZSM-5 zeolites from the perspective of reaction kinetic and diffusion. Their results indicated that when product molecules within the HZSM-5 micropores influence the effective diffusion coefficient, the existence of intracrystalline diffusion limitations can only be accurately revealed by examining the dependence of the reaction rate on crystal size in materials where other catalyst properties (such as H^+ site density) remain constant. In other words, the diffusion limitations of the organic phase within HZSM-5 zeolites play a critical regulatory role in the rate and selectivity of propylene oligomerization, while the composition of the organic phase within the micropores is sensitive to the H^+ site density. This offers new possibilities for regulating the rate and selectivity of propylene oligomerization over H-MFI zeolites. Li et al.^[21] utilized Resonant Soft X-ray Diffraction (RSXRD) and DFT calculations to investigate the locations of isolated aluminum atoms and aluminum pairs within the HZSM-5 structure and the adsorption properties of their corresponding acid sites. It was found that isolated aluminum atoms are mainly distributed in the straight channels, while aluminum pairs are primarily located at the intersections of the straight and sinusoidal channels. Rzepla et al.^[14] probed the distribution patterns and periodic arrangement of aluminum atoms in the ZSM-5 framework using Aluminum K-edge Anomalous X-ray Powder Diffraction (AXRPD). Since the position of aluminum determines the distribution of acid sites, they correlated these acid site distributions with the catalytic activity for propylene oligomerization. Their research revealed that aluminum elements are mainly concentrated at the T-sites at the channel intersections. At single aluminum acid sites, propylene adsorption leads to the faster formation of hydrogen-bonded species and alkoxy species, whereas oligomerization products are more likely to stabilize on

aluminum pairs and their associated proton sites, providing important clues for the study of the catalytic mechanism. Evidently, the density and distribution of acid sites in HZSM-5 molecular sieves have a significant impact on the activity, selectivity, and product distribution of the propylene oligomerization reaction.

In this paper, HZSM-5 zeolites with different Si/Al ratios (Si/Al=30–120) were synthesized using a hydrothermal synthesis method. By regulating the Si/Al ratio of the zeolites, H-type ZSM-5 zeolites were obtained with different acid densities while maintaining analogous pore structures. The acidity and acid density distribution of the HZSM-5 catalysts were comprehensively characterized. The influence of different acid density distributions on the reaction network associated with propylene oligomerization-including olefin oligomerization, cyclization, aromatization, and hydrogen transfer was systematically investigated over HZSM-5 zeolites. This work investigates the regulatory mechanism of HZSM-5 Si/Al ratio modulation on the product distribution of propylene oligomerization.

1 Experimental

1.1 Catalyst preparation

A series of Na-type ZSM-5 zeolites with different Si/Al ratios were prepared *via* hydrothermal synthesis using tetraethyl orthosilicate (TEOS) and sodium aluminate as raw materials, and tetrapropylammonium hydroxide (TPAOH) as the template. A gel system was formed with a molar composition of $\text{SiO}_2:\text{XAl}_2\text{O}_3:0.033\text{NaOH}:0.15\text{TPAOH}:30\text{H}_2\text{O}$, where the aluminum content was systematically adjusted ($X=0.0286, 0.02, 0.0105$ and 0.0083). The resulting products were calcined at $550\text{ }^\circ\text{C}$ for 4 h to remove the template, followed by ammonium ion exchange three times and calcination at $550\text{ }^\circ\text{C}$ for 4 h. Finally, hydrogen-form HZSM-5 zeolites with Si/Al ratios of 30, 50, 90 and 120 were obtained (designated HZSM-5-30, HZSM-5-50, HZSM-5-90 and HZSM-5-120).

1.2 Catalyst characterization

The crystal structure of the zeolites was characterized by X-ray diffraction (XRD) using a Bruker D8 ADVANCE diffractometer (Cu $K\alpha$ source, $\lambda = 0.154\text{ nm}$, voltage 30 kV, current 15 mA), with a scanning range of $5^\circ\text{--}40^\circ$ (2θ) and a scanning rate of $4^\circ/\text{min}$. Scanning Electron Microscopy (SEM) characterization was performed using a Zeiss Gemini360 (Germany) cold field emission scanning electron microscope with a working voltage of 5 kV; samples were sputter-coated with gold to enhance conductivity. The elemental composition of the catalysts was determined using a Rigaku ZSX Primus IV X-ray fluorescence (XRF) spectrometer to ascertain the actual Si/Al ratios.

Nitrogen physisorption tests were conducted using a Microtrac MRB Belsorp Max X analyzer (Japan). Samples were vacuum pretreated at 200 °C for 6 h prior to testing. The adsorption data obtained at −196 °C were calculated using the BET method and the *t*-plot method to determine the specific surface area and micropore volume of the catalysts, respectively.

To quantitatively characterize the acid amount and acid strength distribution of the catalysts, the temperature programmed desorption of ammonia (NH₃-TPD) technique was employed. The tests were conducted on a Belcat II & Belmass II chemisorption analyzer from Microtrac MRB, Japan. The specific procedure was as follows: First, 0.1 g of the sample was pretreated in an Ar stream at 550 °C for 2 h to clean the surface. Subsequently, the sample was saturated with a 10% NH₃/He gas mixture at 50 °C, followed by purging with Ar to remove weakly adsorbed NH₃. Finally, the temperature was programmed to rise to 800 °C at a rate of 10 °C/min in an Ar atmosphere. The desorbed NH₃ signal was continuously monitored using a thermal conductivity detector (TCD) to obtain the NH₃-TPD profile reflecting the acidic characteristics of the samples.

To distinguish and quantify the Brønsted (B) acid and Lewis (L) acid sites in HZSM-5 molecular sieves, pyridine adsorption infrared spectroscopy (Py-FTIR) analysis was conducted. The characterization was performed using a Bruker Vertex 80V spectrometer. First, 20 mg of the sample was pressed into a wafer and pretreated *in situ* under high vacuum (<10^{−1} Pa) at 350 °C for 2 h to clean the surface. Subsequently, pyridine adsorption was carried out at room temperature, followed by evacuation to remove the physisorbed pyridine. Finally, infrared spectra were collected at 150 °C. Quantitative calculations were performed based on the characteristic absorption peaks resulting from the interaction of pyridine with Brønsted acid (1540 cm^{−1}) and Lewis acid (1450 cm^{−1}) sites, using the method described in the literature^[25], to obtain distribution information for both types of acid sites.

1.3 Catalytic reaction test

The oligomerization reaction was performed in a continuous flow fixed-bed reactor with an inner diameter of 10 mm. First, approximately 1 g catalyst particles (40–60 mesh) was mixed with an equal volume of quartz sand of the same mesh size and loaded into the isothermal zone of the reaction tube. Pretreatment was conducted at 500 °C under an argon flow (20 mL/min) for 4 h. Upon completion, the temperature was cooled to the target reaction temperature. Liquid propylene was delivered *via* a liquid metering pump at a flow rate of 0.15 mL/min into a preheater at 180 °C for vaporization and was subsequently introduced into the reactor by the flowing argon carrier gas. The propylene oligomerization reaction was conducted at a pressure of 4.0 MPa, with the liquid hourly space velocity (LHSV) maintained at 4 h^{−1}. To prevent the condensation and retention of heavy oil phases within the system,

oligomerization products were first collected in a hot trap at 200 °C, followed by condensation in an ice water trap. Liquid C₃⁺ products were analyzed using an FID (flame ionization detector) equipped Agilent 7820A gas chromatograph (DB-1 capillary column, 60 m × 530 μm × 25 μm). The product distribution was analyzed using a Shimadzu GCMS-QP2010 gas chromatography mass spectrometry (GC-MS) system. The tail gas composition was monitored online using an Agilent 7890A GC (HP-AL/S column, 30 m × 530 μm × 25 μm) with an FID. To complete the mass balance, uncondensed gases were quantified using a wet gas meter. Only experimental data with a mass balance yield of 95% or higher were included in the discussion. The liquid product yield was calculated as the ratio of the mass of the collected liquid to the total mass of propylene entering the reactor.

2 Results and discussion

2.1 Physicochemical properties of the catalysts

Figure 1 shows the XRD patterns of the hydrothermally synthesized HZSM-5 catalysts with different Si/Al ratios. As shown in the figure, the catalysts with different Si/Al ratios all exhibit characteristic diffraction peaks of ZSM-5 zeolites at $2\theta = 7.5^\circ, 8.8^\circ, 23.0^\circ, 23.9^\circ$ and 24.4° ^[26], confirming that the synthesized catalyst samples all possess a high-purity MFI topology.

Figure 2 displays the scanning electron microscopy (SEM) images of four HZSM-5 zeolites with different silicon to aluminum ratios. As can be seen from Figure 2, the four zeolites (HZSM-5-30, -50, -90, -120) all exhibit a characteristic hexagonal prismatic morphology with well-dispersed crystallites. The slight difference lies in the fact that the low Si/Al ratio catalyst samples, HZSM-5-30 and HZSM-5-50, exhibit small-grain twinning on their surfaces^[27]. As the Si/Al ratio increases, the occurrence of small-grain twinning becomes less pronounced, and almost no small-grain twinning is observed on the surface of the HZSM-5-120 catalyst sample.

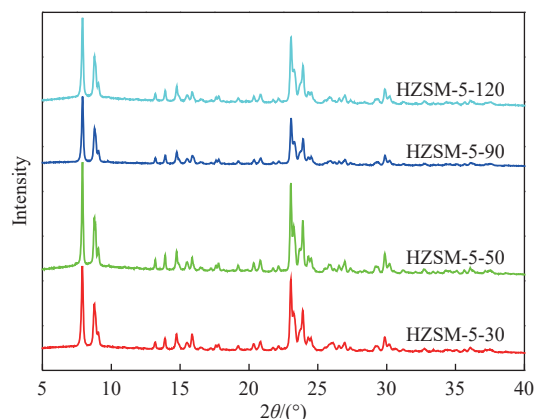
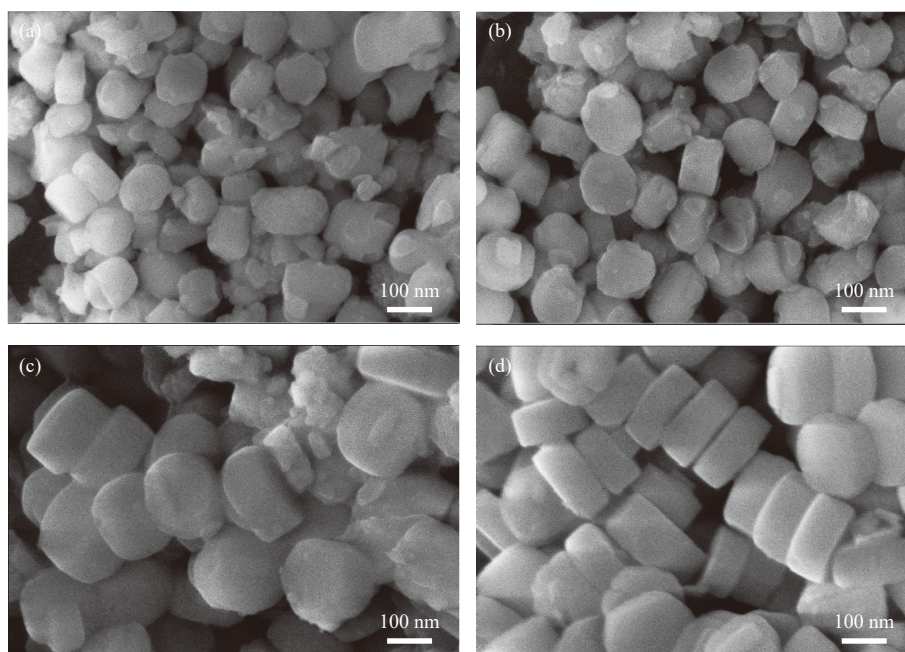


Fig. 1 XRD patterns of HZSM-5 catalysts with varying Si/Al ratios



(a): HZSM-5-30; (b): HZSM-5-50; (c): HZSM-5-90; (d): HZSM-5-120.
Fig. 2 SEM of HZSM-5 catalysts with different Si/Al ratios

Based on the N_2 adsorption-desorption isotherms of HZSM-5 molecular sieves with different Si/Al ratios shown in Figure 3, all samples (HZSM-5-30, -50, -90 and -120) exhibit rapid nitrogen adsorption in the low relative pressure region. This behavior accords with the micropore filling characteristics of Type I isotherms, indicating the presence of a well-developed microporous system. In the high relative pressure region, a distinct hysteresis loop appears, which is classified as a Type H4 hysteresis loop. This type of loop is typically associated with slit-like mesopores formed by the stacking of plate-like particles or intercrystalline pores resulting from the aggregation of nanoscale crystallites. It may also partially originate from silanol nest defect sites on the external surface of the crystals^[27].

The textural properties of HZSM-5 molecular sieves with different Si/Al ratios are summarized in Table 1. As shown in Table 1, with increasing Si/Al ratios, the specific surface areas of the HZSM-5 molecular sieves range from 323.28 to 376.99 m^2/g , and the pore volumes range from 0.24 to 0.41 cm^3/g . The specific surface areas and pore volumes varied within a narrow range, indicating that the regulation of the Si/Al ratio successfully maintained the comparability

of the physical structure of the molecular sieves. Consequently, in the subsequent evaluation of propylene oligomerization performance, differences in catalytic performance can be primarily attributed to variations in acid sites rather than interferences from factors such as mass transfer and diffusion. This provides a reliable experimental basis for accurately establishing the structure-activity relationship between “Si/Al ratio (acidity) and catalytic performance”.

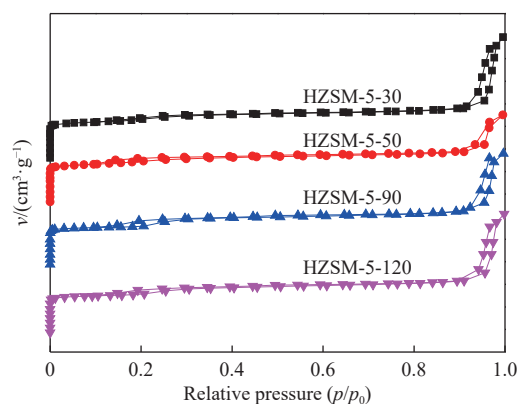


Fig. 3 BET of HZSM-5 catalysts with different Si/Al ratios

Table 1 Textural and physical properties of the catalysts with different Si/Al ratios

Sample	Si/Al ratio	Specific surface area/($m^2 \cdot g^{-1}$)			Pore volume/($cm^3 \cdot g^{-1}$)		
		S_{BET}	S_{Micro}	S_{Ext}	V_{Total}	V_{Micro}	V_{Meso}
HZSM-5-30	34.2	330.78	289.04	23.66	0.41	0.11	0.24
HZSM-5-50	45.2	344.92	307.09	21.62	0.24	0.12	0.10
HZSM-5-90	94.7	376.99	288.54	23.02	0.37	0.11	0.23
HZSM-5-120	117.9	323.28	283.14	23.93	0.40	0.11	0.23

2.2 Acid properties

The NH_3 -TPD profiles of HZSM-5 molecular sieve samples with different Si/Al ratios are illustrated in Figure 4, and the calculated acidity results based on these profiles are listed in Table 2. In the NH_3 -TPD profiles, desorption peaks located below 200 °C correspond to the desorption of NH_3 from weak acid sites. Peaks located between 300 and 500 °C are attributed to NH_3 desorption from medium-strong acid sites, and peaks located above 500 °C are assigned to NH_3 desorption from strong acid sites^[7,27]. As shown in Figure 4, none of the four samples (HZSM-5-30, HZSM-5-50, HZSM-5-90 and HZSM-5-120) exhibit peaks in the high-temperature region, indicating the absence of ultra-strong acid sites. Instead, the catalysts primarily possess weak and medium-strength acidity. The acidity properties exhibit distinct differences as the Si/Al ratio changes. The NH_3 -TPD desorption curves of the HZSM-5-30 and HZSM-5-50 catalysts display a significant bimodal distribution, with peaks centered at 150 and 380 °C, respectively. This indicates that the HZSM-5-30 and HZSM-5-50 catalysts primarily contain weak and medium-strong acid sites. Their weak acid amounts are 599.09 and 448.0 mmol/g, respectively, while their medium-strong acid amounts are 162.12 and 181.2 mmol/g, respectively.

As the Si/Al ratio increases, the total acidity of the molecular sieves decreases significantly, dropping to 212.18 and 136.54 mmol/g for HZSM-5-90 and HZSM-5-120, respectively. Furthermore, the NH_3 desorption temperatures for both types of sites shift toward lower values.

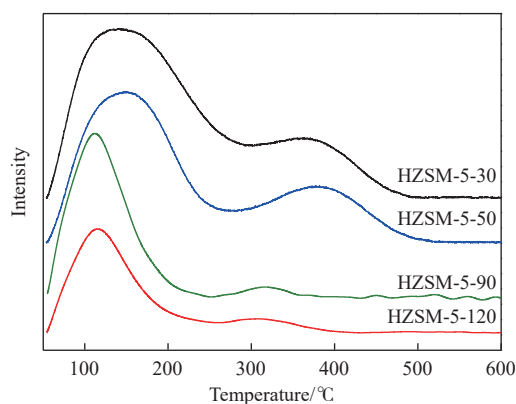


Fig. 4 NH_3 -TPD of HZSM-5 catalysts with different Si/Al ratios

Specifically, the weak acid peak shifts from 150 to 100 °C, and the medium-strength peak shifts from 380 °C to approximately 300 °C. This trend indicates that HZSM-5 catalysts with lower Si/Al ratios exhibit relatively higher acid strength. This phenomenon can be attributed to the higher aluminum content and consequent higher acid density in low Si/Al HZSM-5, which leads to the cooperative adsorption of NH_3 on multiple acid sites, resulting in higher NH_3 desorption temperatures^[27–28].

Figure 5 presents the Py-FTIR spectra of HZSM-5 catalysts with varying Si/Al ratios. The characteristic absorption bands located at 1543 and 1440 cm^{-1} are attributed to pyridine chemisorbed on Brønsted acid (B) sites and Lewis acid (L) sites, respectively. Additionally, the absorption peak at 1447 cm^{-1} corresponds to the characteristic vibration of pyridine molecules adsorbed on extra-framework aluminum species. A comparison of the quantitative Py-FTIR results (Table 2) for HZSM-5 catalysts with different Si/Al ratios reveals that both the amount of Brønsted acid and Lewis acid decrease significantly with increasing Si/Al ratio. Specifically, the Brønsted acid amount decreased from 214.16 (HZSM-5-30) to 46.46 mmol/g (HZSM-5-120), while the Lewis acid amount decreased from 551.86 (HZSM-5-30) to 135.09 mmol/g (HZSM-5-120). As indicated in Figure 5, the Lewis acidity of HZSM-5 zeolites with different Si/Al ratios is composed of medium-strong Lewis acid sites formed by extra-framework aluminum (1447 cm^{-1}) and weak Lewis acid sites formed by silanol groups (1440 cm^{-1}). Consequently, variations in the Si/Al ratio influence the quantity and form of surface hydroxyl groups on the molecular sieve, thereby affecting the acidity of the catalyst.

2.3 Propylene oligomerization performance

Figure 6 compares the propylene oligomerization performance over four HZSM-5 catalysts with different Si/Al ratios (HZSM-5-30, HZSM-5-50, HZSM-5-90 and HZSM-5-120) across a range of reaction temperatures. As illustrated in Figure 6, the liquid product yield for all catalysts initially increases and then decreases with increasing reaction temperature, following a typical volcano trend. However, the optimal reaction temperature is strongly dependent on the Si/Al ratio.

Table 2 Acidity of HZSM-5 catalysts with different Si/Al ratios

Catalyst	Acidity by strength ^a /(mmol·g ⁻¹)			Acidity by type ^b /(mmol·g ⁻¹)		
	weak	medium strong	total	Brønsted	Lewis	total
HZSM-5-30	599.09	162.12	761.21	214.16	551.86	766.03
HZSM-5-50	448.0	181.2	630.56	195.42	428.89	624.31
HZSM-5-90	183.05	23.32	212.18	75.55	182.00	257.55
HZSM-5-120	120.35	7.92	136.54	46.46	135.09	181.56

^a: Acid density from NH_3 -TPD; ^b: Brønsted and Lewis acid densities from Py-FTIR.

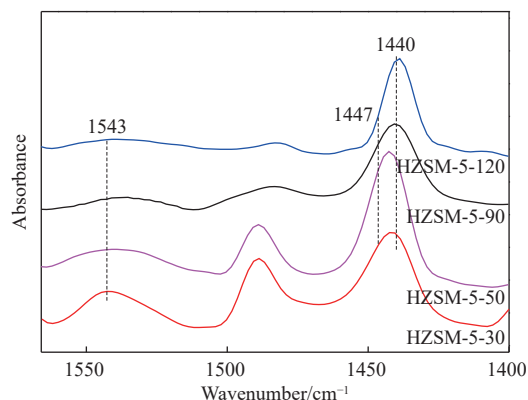


Fig. 5 Py-FTIR profiles of HZSM-5 catalysts with different Si/Al ratios

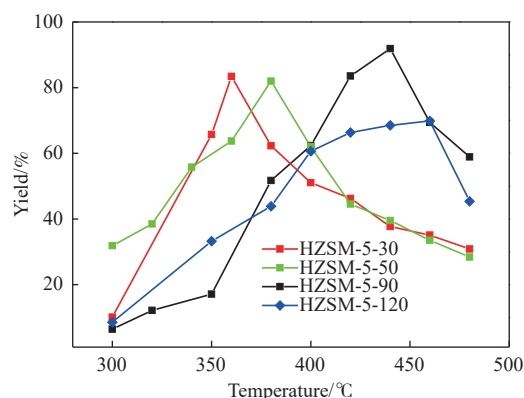


Fig. 6 The propene oligomerization catalytic tests of HZSM-5 catalysts with varying Si/Al ratios

Specifically, HZSM-5-30, HZSM-5-50, HZSM-5-90 and HZSM-5-120 achieved their maximum liquid oil yields of 83.4%, 82.0%, 91.8% and 69.83% at 360, 380, 440 and 460 °C, respectively. Combined with the acidity characterization results discussed earlier, propylene oligomerization is primarily an acid-catalyzed reaction dependent on the acid density of the catalyst. Catalysts with lower Si/Al ratios possess higher acidity, resulting in a lower reaction temperature required to achieve the optimal liquid oil yield.

Figure 7 illustrates the product composition and carbon

number distribution of propylene oligomerization over four HZSM-5 catalysts with different Si/Al ratios at their optimal reaction temperatures (360, 380, 440 and 460 °C, respectively). Propylene oligomerization is often accompanied by side reactions such as hydrogen transfer, cyclization, aromatization, and cracking. As observed in Figure 7 the carbon number distribution across all four catalysts remains primarily concentrated in the C₅–C₁₀ range. This indicates that the products are mainly the result of further cracking and polymerization reactions derived from propylene dimerization and trimerization.

However, the types of reaction products are significantly influenced by the variation in the Si/Al ratio. For the low Si/Al ratio catalysts (HZSM-5-30 and HZSM-5-50), olefins are the dominant products (~79.9% and 82.4%, respectively), followed by smaller fractions of cycloalkanes and alkanes. Notably, no aromatic hydrocarbons were detected for these samples. This can be attributed to the high acid site density and lower operating temperatures, which kinetically favor the primary oligomerization pathway over complex dehydrocyclization^[25].

In contrast, the high Si/Al ratio catalysts (HZSM-5-90 and HZSM-5-120) yield a more diverse product distribution, with alkanes and cycloalkanes each accounting for approximately 25%–30% of the total. However, there are distinct differences in their olefin and aromatic contents. The olefin contents in the reaction products of HZSM-5-90 and HZSM-5-120 are 29.58% and 14.78%, respectively, while the aromatic contents are 23.78% and 14.48%, respectively. In summary, the decrease in acidic site density associated with a higher Si/Al ratio corresponds to an increase in the reaction temperature for optimal liquid oil yield. This elevated reaction temperature promotes the further conversion of propylene and its primary oligomerization products through secondary reactions such as cyclization, aromatization, and hydrogen transfer. Therefore, by synergistically regulating the Si/Al ratio (acidity) of the HZSM-5 catalyst and the reaction temperature, the reaction pathway can be effectively guided to achieve selective regulation of the liquid fuel components in the propylene oligomerization products.

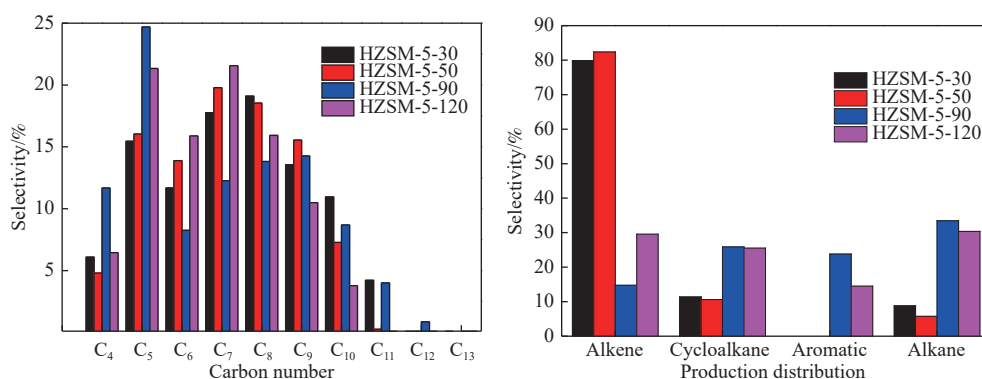


Fig. 7 Produce distribution from propene oligomerization over HZSM-5 catalysts with varying Si/Al ratios

3 Conclusion

In this study, a series of HZSM-5 catalysts with Si/Al ratio of 30, 50, 90 and 120 were prepared *via* a hydrothermal synthesis method to investigate the influence of acid site density on propylene oligomerization. Detailed characterization of the acid type, strength, and density was correlated with catalytic performance to elucidate the regulatory mechanisms governing the reaction pathways. The results indicate that HZSM-5 catalysts with low Si/Al ratios possess a greater number of medium-strength acid sites, which significantly facilitates low-temperature propylene oligomerization while effectively suppressing aromatization and hydrogen transfer reactions. In contrast, HZSM-5 catalysts with high Si/Al ratios, due to their lower acid density, provide more ample surface space and longer residence time for propylene and its reaction intermediates. This promotes the tendency for secondary reactions such as cyclization, aromatization, and hydrogen transfer, ultimately broadening the range of product distribution. This work provides critical insights for the rational design of high-performance catalysts and established a fundamental understanding of how acid site density can be leveraged to tune the selectivity of liquid fuel components in olefin upgrading processes.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] LIU L, YAO W, XIE Y, et al. Research progress on the polymerization of propylene into low carbon olefins[J]. Refin Chem Ind, 2024, 35(4): 18–23.
- [2] CONRAD M. A, DELINE J E, MILLER J T. High-temperature conversion of olefins to liquid hydrocarbons on γ - Al_2O_3 [J]. Ind Eng Chem Res, 2023, 62(12): 4840–4850.
- [3] AGIRREZABAL-TELLERIA I, IGLESIA E. Mechanistic insights and consequences of intrapore liquids in ethene, propene, and butene dimerization on isolated Ni^{2+} sites grafted within aluminosilicate mesopores[J]. J Catal, 2020, 389: 690–705.
- [4] OLIVEIRA P, BORGES P, RAMOS PINTO R, et al. Light olefin transformation over ZSM-5 zeolites with different acid strengths – A kinetic model[J]. Appl Catal A: Gen, 2010, 384(1/2): 177–185.
- [5] XUE Z, ZHANG T, MA J, et al. Accessibility and catalysis of acidic sites in hierarchical ZSM-5 prepared by silanization[J]. Microporous Mesoporous Mater, 2012, 151: 271–276.
- [6] MONAMA W, MOHIUDDIN E, THANGARAJ B, et al. Oligomerization of lower olefins to fuel range hydrocarbons over texturally enhanced ZSM-5 catalyst[J]. Catal Today, 2020, 342: 167–177.
- [7] LI X, HAN D, WANG H, et al. Propene oligomerization to high-quality liquid fuels over Ni/HZSM-5[J]. Fuel, 2015, 144: 9–14.
- [8] FUCHS C, ARNOLD U, SAUER J. Synthesis of sustainable aviation fuels via (co-)oligomerization of light olefins[J]. Fuel, 2025, 382: 133680.
- [9] LASHCHINSKAYA ZN, GABRIENKO A A, STEPANOV A G. Mechanisms of light alkene oligomerization on metal-modified zeolites[J]. ACS Catal, 2024, 14(7): 4984–4998.
- [10] OCCELLI M L J T H, GALAYA L G. Propylene oligomerization over molecular sieves: Part i. zeolite effects on reactivity and liquid product selectivities[J]. J Mol Catal, 1985, 32: 377–390.
- [11] SERGIO VERNUCCIO E E B R G, BROADBELT L J. Propene oligomerization on beta zeolites: Development of a microkinetic model and experimental validation[J]. J Catal, 2021, 395: 302–314.
- [12] ZI Z, LI B, GE Y, et al. Research on propene oligomerization reaction over the Fenton's reagent modified ZSM-5[J]. J Fuel Chem Technol, 2020, 48(8): 986–992.
- [13] SARAZEN M L, DOSKOCIL E, IGLESIA E. Catalysis on solid acids: Mechanism and catalyst descriptors in oligomerization reactions of light alkenes[J]. J Catal, 2016, 344: 553–569.
- [14] PRZEMYSŁAW R, JIRI DEDECEK T. H. E. T, MILAN B, et al. Aluminum distribution and active site locations in the structures of zeolite ZSM-5 catalysts[J]. Science, 2025, 388: 423–428.
- [15] GIL-CALVO M, BARRIO I, LÁZARO J, et al. Assessment of the reaction phase on the oligomerization of 1-butene into solvent range olefins using MFI catalysts[J]. Chem Eng Sci, 2023, 281: 119146.
- [16] TABERNILLA Z, ATEKA A, AGUAYO AT. et al. Low-pressure oligomerization of diluted ethylene on a HZSM-5 zeolite catalyst[J]. J Clean Prod, 2024, 441: 141072.
- [17] WILSHIER K G, SMART P, WESTERN R, et al. Oligomerization of propene over H-ZSM-5 zeolite[J]. Appl Catal, 1987, 31: 339–359.
- [18] QIN L, GAO Y, TANG Y. Progress in synthesizing important chemical products via selective oligomerization [J]. Chem World, 2023, 64(6): 377–389.
- [19] ESCOLA J M, R V G, MORENO J, RODRÍGUEZ R. Liquid-phase-oligomerization-of-1-hexene-using-al-mts-catalysts[J]. Ind Eng Chem Resm, 2006, 45: 7409–7414.
- [20] LI C, DU J, WANG H, et al. A hemicellulose modified HZSM-5 and their application in the light olefins oligomerization to high-quality liquid fuels reaction[J]. Catal Commun, 2017, 102: 89–92.
- [21] LI G, F C FAN, ZHENG M, WANG Q, et al. Atomic locations and adsorbate interactions of Al single and pair sites in H-ZSM-5 zeolite[J]. Science, 2025, 387: 383–393.
- [22] BICKEL E E, LEE S, GOUNDER R. Influence of brønsted acid-site density on reaction-diffusion phenomena that govern propene oligomerization rate and selectivity in MFI zeolites[J]. ACS Catal, 2023, 13(2): 1257–1269.
- [23] LI B, SHAO J, LI S, et al. Study on a novel Zn-containing HZSM-5 catalyst for ethylene aromatization[J]. Fuel, 2025, 397: 135383.
- [24] MLINAR A N, BAUR G B, BONG G G, et al. Propene oligomerization over Ni-exchanged Na-X zeolites[J]. J

- Catal, 2012, 296: 156–164.
- [25] LI B, SHAO J, FENG, et al. Influence of temperature on the catalytic behavior's of Zn-containing HZSM-5 catalysts for ethylene aromatization[J]. J Fuel Chem Technol, 2025, 53(9): 1354–1363.
- [26] LI C, WANG H, ZHU S, et al. Research on butene oligomerization reaction over the hemicellulose modified HZSM-5[J]. J Fuel Chem Technol, 2017, 45(9): 1088–1094.
- [27] MA, X, YANG J, ZHOU J, et al. Synthesis of small crystal ZSM-5 zeolite by solvent-free method and catalytic cracking performance of butene[J]. J Fuel Chem Technol, 2025, 53(1): 163–173.
- [28] ZHEN J, QIN K, QIN Y, et al. Interaction mechanism of Brønsted acid sites and basic molecules in HMF zeolites[J]. J At Mol Phys, 2025, 42(4): 041001.

酸性对 HZSM-5 催化剂上丙烯齐聚反应性能的影响

李 薇^{1,2}, 王 辉^{2,3,*}, 张金芝^{2,3}, 徐 玺^{2,3}, 郭星翠^{2,3}, 焦甜甜^{1,*}, 吴晋沪^{2,3}

(1. 山东科技大学 化学与生物工程学院, 山东 青岛 266590; 2. 中国科学院青岛生物能源与过程研究所, 山东 青岛 266101; 3. 山东能源研究院, 山东 青岛 266101)

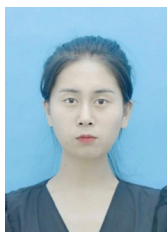
摘 要: 水热合成了不同硅铝比的 HZSM-5 分子筛催化剂, 采用 XRD、SEM、N₂ 物理吸附-脱附、NH₃-TPD 等分析了催化剂结构、组成及酸性, 比较研究了不同硅铝比(30、50、90 和 120)催化剂上丙烯齐聚反应的催化性能。结果表明, 随着硅铝比的增加, 催化剂的酸性有所降低, 丙烯齐聚反应得到液体燃料油收最大反应温度有所提升, 分别为 360、380、440 和 460 °C。探讨了硅铝比不同的 HZSM-5 分子筛酸性与丙烯齐聚反应产物分布以及反应路径的关联。研究表明, 低硅铝比的 HZSM-5 分子筛, 酸性密度大, 有助于丙烯齐聚反应的发生, 反应产物主要为烯烃; 而高硅铝比 HZSM-5 催化剂更有利于丙烯及丙烯齐聚初级烯烃产物的进一步环化、芳构化以及氢转移等反应的发生, 产物分布范围扩大, 包含烯烃、环烷烃芳烃以及烷烃。

关键词: HZSM-5; 丙烯; 齐聚; 酸性

中图分类号: O643

文献标识码: A

作者简介:



李薇(1999), 硕士研究生, 研究方向为丙烯齐聚制高附加值化学品催化反应研究, 18456450620@163.com。



王辉(1980), 博士, 副研究员, 研究方向为煤/生物质基碳资源催化转化, wang_hui@qibebt.ac.cn。