

Review Paper

Progress and perspectives on ZSM-22-based catalysts for long-chain *n*-alkane hydroisomerization

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ABSTRACT

Hydroisomerization of long-chain *n*-alkanes holds significant value in pour point reduction and quality enhancement of fuels, the development of premium lubricants, and the industrial advancement of biofuels. Among various catalysts, ZSM-22 zeolite has emerged as an ideal support due to its unique pore structure and tunable acidity. This review summarizes the latest research progress on ZSM-22-based bifunctional catalysts. Studies have shown that two main strategies are commonly employed to enhance isomerization performance: optimizing the hydrogenation/dehydrogenation functionality of metal sites and tailoring the physicochemical properties of the zeolite. High-quality metal function contributes to an ideal bifunctional catalytic mechanism, which can be achieved by precisely controlling the dispersion, location, and exposed crystal facets of noble metals (e.g., Pt, Pd). While non-noble metals (e.g., Ni) can show hydroisomerization performance rivaling noble metals, their development relies on constructing bimetallic sites and carefully balanced metal-support interactions. In terms of ZSM-22 functional modification, reducing crystal size and constructing hierarchical pore structures are effective in mitigating the diffusion limitations imposed by its micropores on alkanes and olefinic intermediates. Meanwhile, acidity modulation can be achieved via framework heteroatom incorporation, ion exchange, surface acid site passivation, and partial pore blockage. Additionally, co-crystallization and composite zeolite strategies offer promising pathways for further enhancing the isomerization performance of ZSM-22-based catalysts. This review aims to provide both theoretical insights and technical guidance for the development of efficient catalysts for long-chain *n*-alkane hydroisomerization, offering value to researchers new to this field.

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1. Introduction

Currently, hydrocarbon-based fuels such as gasoline, diesel, and jet fuel remain the primary energy sources for industrial and transportation sectors. Table 1 summarizes the performance specifications of several representative fuel types. However, fuels produced from conventional petroleum reforming processes and coal or natural gas conversion technologies centered around

Fischer-Tropsch synthesis often fall short of meeting modern environmental and performance standards (Wei et al., 2022; Aljajan et al., 2023). As a result, synthetic fuels require further upgrading to optimize their molecular structure. To address this, a range of refining technologies-including catalytic cracking, catalytic hydrogenation, alkylation, and hydroisomerization have been developed and widely applied.

The application of hydroisomerization technology varies depending on the carbon chain length of the alkanes. For light alkanes ($\leq C_7$), isomerization can significantly boost the octane number of gasoline by 50%–90% (Raybaud et al., 2001). In recent years, notable progress has been made in studies using *n*-pentane and *n*-hexane as probe molecules, leading to industrial applications that achieve isomerization yields exceeding 95% (Phan and Lee, 2018; Aljajan et al., 2023). For long-chain alkanes ($\geq C_8$), hydroisomerization serves as a key process for lowering the pour

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Table 1
Parameter indicators of several typical oil products.

Parameter	Category			
	Gasoline	Diesel	Jet fuel	Lubricant
Main carbon number	5–12	10–22	8–16	16–20
Average molar quantity	70–80	310–335	200–250	290–360
Main indicators	Octane number	Cetane number, pour point	Heating value, pour point	Viscosity, pour point
Ideal components	<i>i</i> -Alkane	<i>i</i> -Alkane	Cycloalkane, <i>i</i> -alkane	Mono-branched <i>i</i> -alkane

point of diesel and jet fuel. Moreover, when combined with hydrodeoxygenation, this technology is employed in the deep upgrading of bio-oils, converting them into normal alkanes suitable for use in high-quality fuels (Wang et al., 2019a). Beyond pour point reduction, hydroisomerization of long-chain alkanes also plays an essential role in the production of premium lubricants (Huang et al., 2004). It is worth noting that while diesel and jet fuel benefit from multi-branched isomers, ideal lubricant components are typically mono-branched alkanes, which provide a desirable balance between low-temperature fluidity and appropriate viscosity. However, compared to light alkanes, long-chain alkanes are more prone to C–C bond cleavage, which severely limits the yield of isomerized products. Therefore, suppressing cracking reactions remains a central challenge in enhancing the hydroisomerization performance of long-chain alkanes.

Developing novel bifunctional catalysts is a key strategy for improving alkane isomerization yields. These catalysts typically consist of a small amount of metal component and an acidic support. The metal component, usually selected from Group VIII and VIB elements of the periodic table, provides hydrogenation and dehydrogenation functionality (Li et al., 2017, 2018). The acidic support may include amorphous oxides, solid superacids (such as $\text{Al}_2\text{O}_3\text{--Cl}$, $\text{SO}_4^{2-}/\text{ZrO}_2$, and WO_3/ZrO_2), or zeolites (such as ZSM-22, ZSM-23, SAPO-11, and MOR) (Calero et al., 2004; Liu et al., 2023c). Compared with amorphous oxides and solid superacids, zeolites offer significant advantages due to their unique pore structures and tunable acidity, particularly in terms of shape-selective isomerization, resistance to poisoning, and suppression of coke formation (Bi et al., 2018).

The isomerization performance of zeolite-based catalysts is primarily governed by the balance between metal sites and Brønsted acid sites (BAS)—including their ratio and spatial distribution—as well as the diffusion limitations of alkanes within the zeolite's microporous channels. For instance, Wang et al. (2019a) systematically investigated the effects of the metal/BAS ratio, the distance between the two types of sites, and hierarchical pore structures on catalytic performance. Wei et al. (2022) conducted a comparative study on the differences in metal-acid balance required for the hydroisomerization of short-versus long-chain alkanes and examined how zeolite textural properties affect their performance. Aljajan et al. (2023) used the hydroisomerization of *n*-hexadecane as a model reaction to deeply explore the reaction mechanism and the impact of coke formation on catalyst stability. These studies demonstrate that Pt and Pd are the most widely used metal centers due to their excellent hydrogenation/dehydrogenation capabilities. At the same time, one-dimensional ten-membered ring (1D-10 MR) zeolites have been identified as the most effective acidic supports, thanks to their shape-selective effects derived from the close match between their pore openings and alkane molecular sizes.

ZSM-22 is a representative 1D-10 MR zeolite. Its elliptical pore openings and diverse crystal morphologies—including rod-like, needle-like, lamellar, and granular forms—have been well documented (Song et al., 2025a). With a pore size of approximately $0.46 \text{ nm} \times 0.57 \text{ nm}$, ZSM-22 allows the diffusion of linear alkanes

into its channels while restricting the formation and transport of multi-branched isomers. Moreover, its channel architecture helps suppress olefin oligomerization and aromatization, thereby reducing coke formation (Song et al., 2025c). However, the development of ZSM-22-based bifunctional catalysts with excellent performance still faces several challenges. On the one hand, the extended microporous channels and tendency for crystal aggregation increase the diffusion resistance for alkanes and their intermediates. On the other hand, framework aluminum often gives rise to strong BAS, leading to a mismatch between metal and acid functionalities. As such, functional modification of ZSM-22-based catalysts—via either direct synthesis or post-synthetic treatment—to achieve an optimized metal-acid balance and reduced diffusion resistance has become an important research direction.

In light of these considerations, this review aims to summarize the research progress of ZSM-22-based catalysts in the hydroisomerization of long-chain alkanes, focusing on comparative analyses of representative zeolites, mechanistic insights into the isomerization process, and key areas of current research interest. Through systematic categorization and comparison, this work highlights the strategies for improving catalyst performance and the specific features of various modification approaches. The insights provided herein are intended to offer theoretical and technical guidance for the development of efficient catalysts for long-chain alkane hydroisomerization and to inspire future functional modifications of zeolites with 1D-10 MR pore systems.

2. Comparative analysis of representative zeolites

As both BAS donors and active environments for alkane hydroisomerization, the type of zeolite support has a significant impact on catalytic performance. This section compares ZSM-22 with other representative zeolites, including those featuring one-dimensional (1D) and three-dimensional (3D) channel structures. It has been observed that the catalytic behavior of 1D zeolites is largely governed by their intrinsic physicochemical properties. At low conversion levels, pore mouth dimensions systematically influence the distribution of isomerization versus cracking products. Compared to zeolites with intersecting channels, ZSM-22 demonstrates higher isomer selectivity. Notably, unlike more commonly studied systems for alkane hydroisomerization, the use of ZSM-22 in model fuel conversion has been less explored, and the reactions tend to be more complex—imposing higher demands on catalyst modification strategies.

Although 1D zeolites are widely studied as acidic supports, their catalytic performance varies considerably. Fig. 1 illustrates the channel configuration or geometry of representative 1D channel zeolites. For instance, Zhang et al. (2016) reported that with 0.5 wt% Pt loading, the hydroisomerization activity for *n*-C₁₆ followed the order: ZSM-23 > ZSM-48 > ZSM-22, while the isomer selectivity followed the same trend. Using similar metal loadings and preparation methods, our group (Wang et al., 2024a,b) observed the following activity sequence: ZSM-12 $\approx$ ZSM-23 > ZSM-22 > EU-

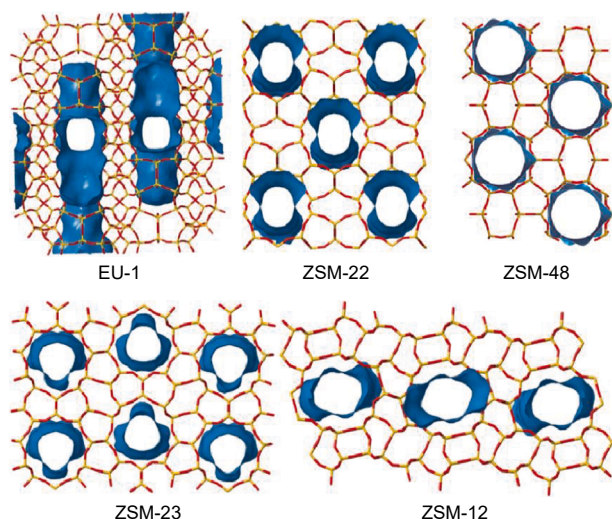


Fig. 1. Illustrations of the channel system of representative 1D channel zeolites.

1 > ZSM-48. Interestingly, ZSM-22 achieved the highest isomer yield (53%), far surpassing that of ZSM-48 (19%), ZSM-23 (11%), EU-1 (27%), and ZSM-12 (33%). Additional studies by Park and Ihm (2000) and Hu et al. (2005) have also reported performance differences among 1D zeolites. These findings indicate that the Si/Al ratio, morphology, and textural properties of 1D zeolites strongly influence their catalytic behavior. Consequently, it is difficult to determine the suitability of a particular zeolite for long-chain alkane hydroisomerization through direct performance comparison alone.

In addition to activity and isomer selectivity, the distribution of products is also a key factor influencing catalyst applicability. Existing studies have shown that in long-chain alkane hydroisomerization, it is difficult to generate isomers with ethyl or longer branches, as these tend to undergo cracking (Mériaudeau et al., 1997; Maesen et al., 1999). For mono-methyl branched isomers (e.g., from n -C₁₆), species such as 2 M- to 7 M-C₁₅ are typically detected, but their distributions vary depending on zeolite pore size. We further analyzed the product distributions of ZSM-22 compared to ZSM-23, ZSM-48, and ZSM-12—all 1D zeolites with varying channel diameters. Given that both isomer and cracking product distributions are significantly influenced by conversion rate and pore architecture, and that thermodynamic equilibrium may distort product profiles at high conversions, the following comparisons were all conducted under conditions where overall conversion remained below 60%.

Due to their shared fundamental building units, the shape-selective differences between ZSM-22 and ZSM-23 have been extensively studied. Gao et al. (2020) found that at 30% conversion, Pt/ZSM-22 tended to cleave C–C bonds near the middle of the n -C₁₂ chain, with C₉ showing the highest cracking selectivity (10.4%). In contrast, Pt/ZSM-23 favored cleavage near the chain ends, with C₅ selectivity reaching 17.5%. When using waxy vacuum gas oil as the feedstock, Pt/ZSM-22 produced over 2% more light products (gas + naphtha) and more than 3% additional heavy base oil than Pt/ZSM-23. Wang et al. (2024a) observed that at 60% n -C₁₆ conversion, ZSM-22 with its larger micropores compared to ZSM-23 enabled the formation of isomers with methyl branches closer to the center of the chain via a “key-lock” mechanism (27.7% vs. 1.77%). The cracking selectivity peaked at C₁₀ (13%) for ZSM-22 and at C₆ (16%) for ZSM-23. Similarly, Chi et al. (2012) using n -C₁₂ as a model compound, showed that ZSM-22 promotes preferential cleavage at the chain ends, with cracking products concentrated around C₅ (~16%) and C₈ (~16%). Under comparable conversions

(~60%), ZSM-23, with its smaller pore size, more readily triggers C–C cleavage at mid-chain positions, with maximum selectivity for C₃ (18%) and C₄ (18%). These findings indicate that compared to ZSM-23, ZSM-22 offers greater selectivity for centrally branched isomers and heavier cracking products.

Unlike the elliptical pore openings of ZSM-22, ZSM-48 features round pores that better accommodate the insertion of alkane molecules. Ge et al. (2024) reported that at 40% n -C₁₂ conversion, Pt/ZSM-48 exhibited much higher selectivity toward 5/6 M-C₁₂ isomers compared to Pt/ZSM-22 (9.3% vs. 2.1%), supporting the “key-lock” isomerization mechanism. The maximum cracking selectivity was observed at C₄ (27%) for Pt/ZSM-22 and at C₉ (15%) for Pt/ZSM-48. Wang et al. (2021a) prepared ZSM-22 and ZSM-48 with similar Si/Al ratios and confirmed that at ~20% conversion, ZSM-22 showed higher selectivity toward 2/3 M-C₁₂ (36% vs. 28%), while ZSM-48 exhibited higher selectivity for 5/6 M-C₁₂ (25% vs. 14%). Zhang et al. (2016) noted that at n -C₁₆ conversions below 30%, both ZSM-48 and ZSM-22 primarily promoted terminal methyl isomerization, with similar selectivity for 2 M-C₁₅ (31% vs. 25%). However, ZSM-48 favored 4/5 M-C₁₅ formation (~13%), while ZSM-22 showed nearly no presence of these isomers. These results suggest that ZSM-48 is more conducive to forming centrally branched mono-methyl isomers and selectively produces heavier cracking products.

In contrast to the 10-MR channels of ZSM-22, ZSM-12 features 1D twelve-membered ring pores (0.67 nm × 0.51 nm), which offer lower diffusion resistance for alkanes and intermediates. Han et al. (2023) found that on ZSM-22, mono-branched isomers were always more selectively produced than multi-branched ones, with a peak in selectivity observed as n -C₁₂ conversion increased. Additionally, the carbon number distribution of cracking products shifted toward lighter components at higher conversion. For ZSM-12, multi-branched isomers were consistently more favored than mono-branched, and the cracking products displayed a symmetric distribution—characteristic of large-pore zeolites. Bi et al. (2017) further confirmed that even when ZSM-22 and ZSM-12 possess similar BAS densities, the channel structure of ZSM-22 suppresses the formation of multi-branched isomers and enhances selectivity for mono-branched isodecanes. The larger pore size of ZSM-12, however, allows olefin intermediates to undergo random cleavage, resulting in carbon number distributions of cracking products that are relatively insensitive to temperature.

From the product distributions of the above-mentioned 1D zeolites, it is evident that as the pore size increases from ZSM-23 (0.52 nm × 0.45 nm) to ZSM-48 (0.56 nm × 0.53 nm), the formation of mono-branched isomers with methyl groups positioned at the center of the carbon chain becomes more favorable, while the cracking products tend to shift toward heavier fractions. However, at high conversions (e.g., 90%), the composition of isomerization and cracking products approaches thermodynamic equilibrium, and the influence of zeolite acidity becomes dominant (Phan and Lee, 2018). Typically, stronger acidity results in higher yields of terminal mono-branched isomers and lighter cracking products, as centrally branched isomers and heavy components are more prone to secondary cracking. In contrast to 1D-10 MR zeolites, the pore size of ZSM-12 (0.5–0.62 nm) is slightly larger than that of methyl-branched alkanes, promoting the formation of multi-branched isomers and yielding a more uniform distribution of cracking products.

Interestingly, while 1D zeolites often show significant differences in performance, many studies have found that β zeolites with 3D channel structures exhibit higher activity than ZSM-22, but generally lower isomer selectivity. For example, Batalha et al. (2012) compared Pt/ β and Pt/ZSM-22 in the hydroisomerization of n -C₁₆ and found that although β achieved a

conversion rate 4.6 times higher than ZSM-22, the 1D-10 MR channels of ZSM-22 offered spatial confinement that precisely guided the reaction pathway and suppressed undesired cracking, maintaining 92% isomer selectivity even at 90% conversion. Similarly, Merabti et al. (2010) concluded that although Pt/ZSM-22 had only 40% of the conversion efficiency of Pt/ β , its isomer selectivity was significantly higher. While sodium ion exchange could reduce the acidity of β , its activity remained 2.5 times that of ZSM-22, and its pore architecture was unable to precisely control the location of branching. Chi et al. (2015) reported that for n -C₁₄, the activity order was $\beta > \text{ZSM-23} > \text{ZSM-22} > \text{SAPO-11}$, attributing β 's lower isomer selectivity to its large pores that facilitate the secondary cracking of multi-branched isomers. Besides β , other 3D channel zeolites like ZSM-5 have also been shown to exhibit higher activity but lower isomer selectivity than ZSM-22 under identical metal type and loading conditions (Hu et al., 2005; Mu et al., 2024). This is likely because the intersecting channels in 3D zeolites increase the frequency of contact between alkanes and BAS, but fail to provide the spatial confinement required for selective isomerization.

While laboratory studies often use model alkane reactions, more complex feedstocks—such as model oils—can better reflect the intrinsic catalytic properties of zeolites. Vlasova et al. (2023) investigated the performance of various zeolites in the hydroconversion of methyl palmitate and found the isomer yields followed the trend: ZSM-12 < ZSM-5 < SAPO-11 < ZSM-22. He et al. (2018) showed that Pt/ZSM-22 could directly convert n -decanol into isomerized alkanes in a single step, whereas Pt/ZSM-5, due to its strong acidity, favored side reactions such as aromatization. In contrast, Pt/Al-MCF with its higher mesoporosity was better suited for dehydrating alcohols into olefin intermediates. The observed isomer selectivity order was ZSM-22 > MCF > ZSM-5. Wang et al. (2012) compared Pt/ZSM-22 and Pt/SAPO-11 for the one-step hydroprocessing of triglycerides (reaction pathway shown in Fig. 2), and found that the narrow channels of ZSM-22 hindered the diffusion of bulky intermediates, resulting in higher cracking activity and requiring higher temperatures to achieve similar conversion. Given the high cost of Pt, the group further evaluated Ni/ZSM-22 and Ni/SAPO-11 under the same reaction, arriving at similar conclusions (Wang et al., 2014). These results underscore that the compatibility between model oil molecule size and the ZSM-22 pore structure is key to achieving high isomer selectivity. Nonetheless, the chemical complexity of model oils and the involvement of deoxygenation reactions suggest that further functional tailoring of ZSM-22 is still necessary to enhance its versatility across a broader range of applications.

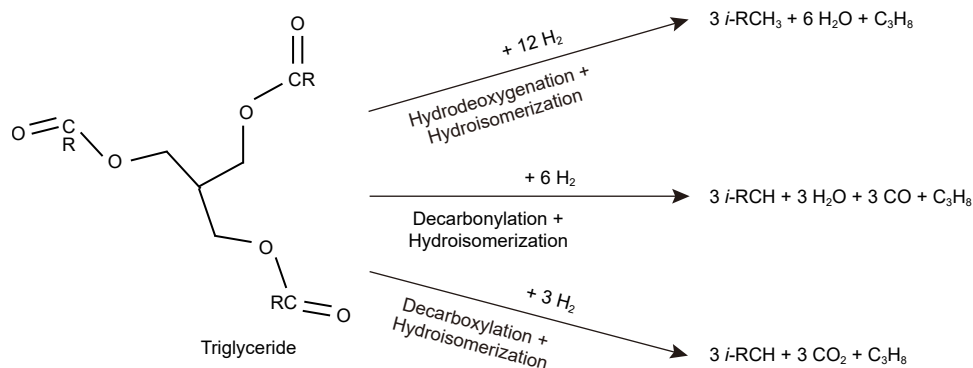


Fig. 2. Plausible reaction pathways combining deoxygenation and hydroisomerization of triglyceride in a single step. Adapted from Wang et al. (2012) with permission from Wiley.

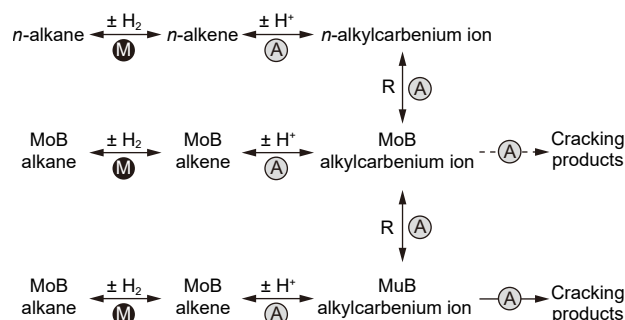


Fig. 3. Reaction network for n -alkanes hydroisomerization over bifunctional catalysts; M-metal sites, A-Brønsted acid sites, R-rearrangement of carbenium ions, MoB-mono-branched, MuB-multibranch. Adapted from ref (Jaroszewska et al., 2019) with permission from Elsevier.

3. Mechanism of long-chain alkane hydroisomerization

A comprehensive understanding of the hydroisomerization mechanism of alkanes is essential for guiding rational catalyst design. Over the course of catalyst development, several mechanistic interpretations have been proposed, including the carbenium ion mechanism, bifunctional mechanism, bimolecular reaction mechanism, hydrogen spillover mechanism, and redox mechanism (Blomsma et al., 1996; Wan et al., 1996; Song et al., 2012; Ma et al., 2018). For ZSM-22-based catalysts, the hydroisomerization of long-chain alkanes is generally considered to follow the bifunctional reaction mechanism (Wang et al., 2011; Wei et al., 2022). Additionally, given the shape-selective nature of ZSM-22 channels, the concepts of pore mouth and key-lock catalysis are often used to explain the distribution of isomeric products (Weisz and Frilette, 1960; Souverijns et al., 1998).

As illustrated in Fig. 3, the hydroisomerization of long-chain alkanes proceeds via the following sequence of steps:

- The alkane is adsorbed onto the metal site and undergoes dehydrogenation to form an olefin.
- The olefin desorbs from the metal site and diffuses to a BAS on the support.
- The olefin is protonated by the BAS to form a carbenium ion.
- The carbenium ion undergoes skeletal rearrangement to yield a mono-branched carbenium ion.
- The mono-branched carbenium ion loses a proton to generate an isomerized olefin of the same carbon number, which diffuses back to the metal site.

- f) The isomerized olefin is then hydrogenated on the metal site to form the final isomerized alkane.

In addition, the mono-branched carbenium ion may continue to undergo further skeletal rearrangement to form multi-branched intermediates or undergo β -scission to produce cracking products. The illustrated pathway represents a single transformation cycle in long-chain alkane hydroconversion. In theory, the products from this initial reaction can undergo similar secondary transformations, forming a complex reaction network.

As shown in Table 2, the cracking activity of carbenium ions increases with the degree of branching. Type A β -scission occurs on tri-branched carbenium ions, resulting in two branched fragments. Type B β -scission involves di-branched carbenium ions and produces one branched and one linear fragment. Type C β -scission generates two linear fragments derived from mono-branched carbenium ions. Unlike type C, type D β -scission yields a carbenium ion located at a primary carbon; however, due to the high energy of the resulting carbenium intermediate, this type of cleavage does not occur with all catalysts. In general, the relative cracking rates follow the order: $A \gg B1 > B2 > C > D$ (Souverijns et al., 1998).

The concept of shape-selective catalysis was first introduced by Weisz and Frillette in 1960 to explain how the structural characteristics of different zeolite catalysts influence product distribution. As illustrated in Fig. 4, Martens et al. (2001) confirmed that the pore mouths of ZSM-22 serve as the active sites for alkane isomerization. Because steric hindrance is inversely proportional to pore size, their study proposed that carbenium ions preferentially undergo skeletal rearrangement at the pore mouths of ZSM-22. Pore mouth selectivity favors the formation of terminal mono-branched isomers, while key-lock selectivity facilitates the generation of centrally branched and multi-branched isomers. Notably, when the carbon number of the alkane exceeds 12, both mechanisms coexist, and the isomer distribution increasingly aligns with the predictions of key-lock catalysis as the chain length increases.

The location of BAS within ZSM-22 has also been shown to significantly influence isomerization performance. Choudhury et al. (2012) applied the SEMK (Single-Event MicroKinetic) model to analyze the yield and distribution of hydroisomerized products from n -C₁₀ over Pt/ZSM-22. Using parameters such as alkane adsorption enthalpy, protonation enthalpy, and BAS density, they evaluated the roles of pore mouth BAS (ps), internal BAS within micropores (mp), and bridging BAS between pore mouths (bs). The results revealed that BAS (mp) promoted the cracking of olefin intermediates, while the cleavage of branched intermediates occurred predominantly on BAS (ps) and BAS (bs). At lower

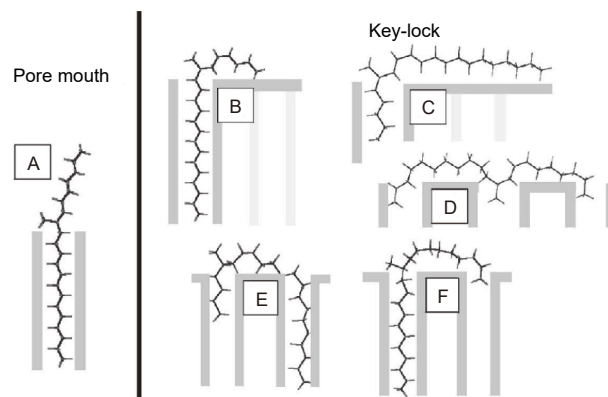


Fig. 4. Pore mouth and key-lock selectivity. Adapted from Martens et al. (2001) with permission from Elsevier.

temperatures (463 K), pore mouth catalysis was dominant. When the temperature was increased to 523 K, the formation of multi-branched isomers became more favorable, with key-lock catalysis taking precedence.

Similarly, as shown in Fig. 5, Wang et al. (2020b) prepared ZSM-22-based catalysts with controlled BAS distribution and density using a template protection and ammonium exchange strategy. In hydroisomerization of n -C₁₂, they found that weak BAS at the pore mouth facilitated the formation of centrally branched mono-isomers, while stronger BAS near the pore entrance favored multi-branched isomer formation. Furthermore, BAS located within the channels and on the external surface of the zeolite promoted (s, p) β -scission of olefin intermediates and (s, s) β -scission of branched olefin intermediates, respectively.

In summary, using n -C₁₆ as an example, the hydroisomerization pathway of n -alkanes over a Pt/ZSM-22 catalyst is illustrated in Fig. 6. Initially, the dehydrogenation of n -C₁₆ on Pt site yields an olefin intermediate, whose subsequent migration to the pore mouth active sites of ZSM-22 is governed by the precise location of the Pt particles (external surface, pore mouth, or internal channels). It is important to note that external BAS on ZSM-22 exhibit no shape selectivity, and for micron-sized ZSM-22 crystals, the vast majority of BAS are located at the pore mouths and within the internal micropores. Under pore mouth shape selectivity, the olefin can be protonated by BAS at the pore mouth to form a mono-branched carbenium ion. At higher conversions, multiple branching can occur through a key-lock mechanism or via successive isomerization steps, leading to the formation of multi-branched carbenium ions. The resulting isomerized olefins

Table 2
 β fracture mechanism of alkyl carbon ion. Adapted from ref Souverijns et al. (1998) with permission from Elsevier.

Type	Minimum carbon number	Carbocation transfer	Sample
A	8	tert $\rightarrow$ tert	
B1	7	sec $\rightarrow$ tert	
B2	7	tert $\rightarrow$ sec	
C	6	sec $\rightarrow$ sec	
D	5	sec $\rightarrow$ prim	

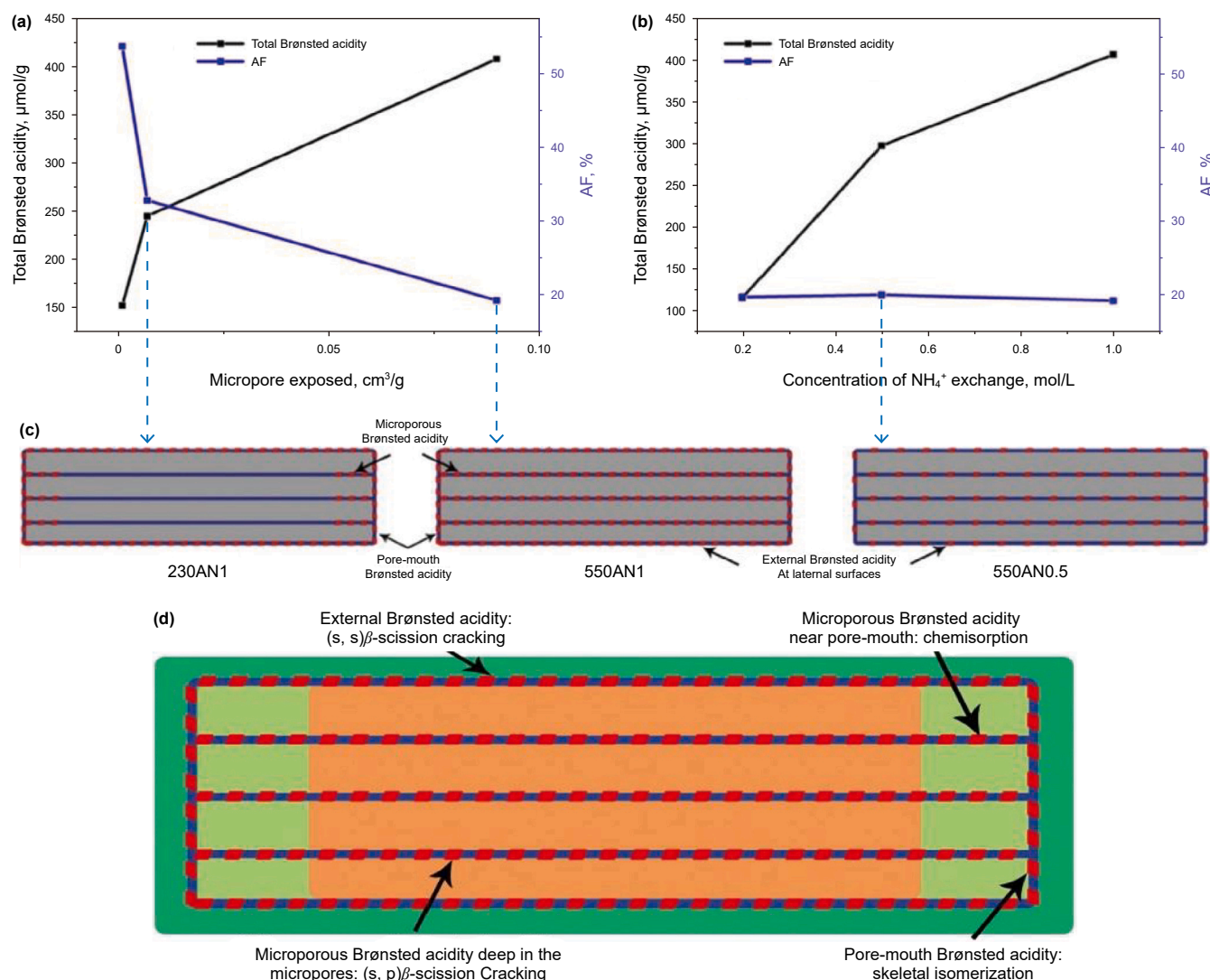


Fig. 5. Pt/ZSM-22 catalysts with different BAS distributions: (a) correlation between micropore exposed of ZSM-22 and total BAS & AF, (b) correlation between NH_4^+ aqueous concentration and total BAS & AF, (c) schematic acidity distribution, (d) the role of BAS at different positions. Accessibility factor (AF) defined as the ratio between the amount of external Brønsted acidity and total Brønsted acidity. Adapted from Wang et al. (2020b) with permission from Elsevier.

(MB = C_{16} , 0.5–0.62 nm; MTB = C_{16} , >0.7 nm), prior to rehydrogenation at the Pt site, may undergo (s, s) β -scission reactions on BAS located at the pore mouth or on the external surface, producing lower-carbon-number olefinic carbenium ions and alkanes. Additionally, olefins that diffuse into the zeolite channels can be protonated by internal BAS to generate hydrocarbon carbenium ions ($n = \text{C}^+_{16}$, 0.43–0.49 nm), which may subsequently undergo (s, p) β -scission reactions, leading to the formation of lower-carbon-number olefins and alkanes.

4. Optimization strategies for metal sites

Research on tuning the metal centers in ZSM-22-based catalysts has primarily focused on the optimization of noble metals and the development of non-noble metal alternatives. Platinum (Pt) and palladium (Pd) are considered ideal choices due to their high hydrogenation/dehydrogenation activity and low hydrocracking tendency. Studies have shown that catalytic performance can be enhanced by adjusting loading conditions and post-treatment methods to optimize metal dispersion, particle size, exposed crystal

facets, and site placement. In an effort to reduce catalyst cost, some researchers have explored the incorporation of non-noble metals (such as Ni and Co) and bimetallic active sites. However, due to the inherently higher hydrocracking activity and differing metal-support interactions associated with non-noble metals, further research is needed to develop effective optimization strategies for these systems.

4.1. Adjustment of noble metals

Pt and Pd are the most commonly used metal sites in bifunctional catalysts. An ideal hydroisomerization catalyst requires a sufficiently high molar ratio between metal sites and BAS ($n(\text{Me}/\text{A})$) to ensure that the acid-catalyzed step of olefin intermediates becomes rate-limiting. Smulders et al. (2024) reported that a Pt loading of at least 0.05 wt% is necessary on Pt/ZSM-22 catalysts to achieve adequate hydrogenation and dehydrogenation activity. Testing with $n\text{-C}_{16}$ showed that when $n(\text{Me}/\text{A}) < 0.18$, the acid function intensifies the cracking of isomerized products, whereas when $n(\text{Me}/\text{A}) > 0.78$, excess Pt particles tend to block the micropores of ZSM-22, severely limiting the diffusion of olefin

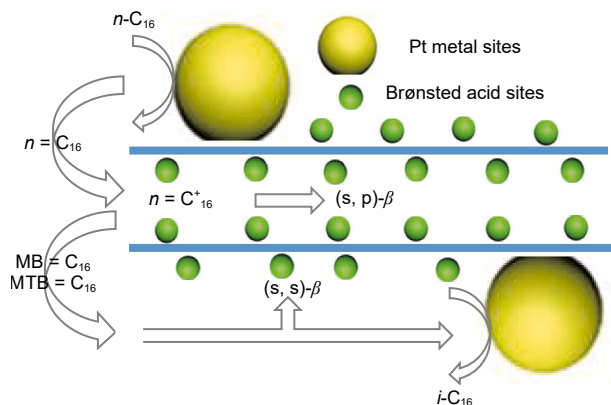


Fig. 6. Possible pathways of n -C₁₆ hydroisomerization over Pt/ZSM-22 catalysts with Pt located on the external surface.

intermediates. Therefore, selecting an appropriate metal loading within a suitable $n(\text{Me}/\text{A})$ range is essential.

At a fixed metal loading, selecting a suitable loading method to control metal location and dispersion is an effective strategy to enhance catalytic performance. Cheng et al. (2020) prepared mixed ZSM-22/Al₂O₃ supports and selectively deposited >75% of 0.5 wt% Pt either inside the zeolite channels (Pt-ZSM-22/Al₂O₃, via ion exchange) or on the alumina surface (Pt-Al₂O₃/ZSM-22, via electrostatic adsorption). Testing with n -C₈ showed that when Pt is located within the zeolite pores, it promotes cracking of olefin intermediates, reducing isomer selectivity. In contrast, when Pt is situated on Al₂O₃, intermediates are more likely to isomerize at external BAS sites on ZSM-22, significantly reducing cracking. Through precise design, Cheng et al. (2022) also demonstrated that when Pt species are predominantly located on the external surface of ZSM-22 crystals, excellent n -C₇ isomerization activity and selectivity can still be achieved even with an ultra-low Pt loading. Wang et al. (2021b) confirmed similar trends using n -C₁₂, with Pt-Al₂O₃/ZSM-22 outperforming Pt-ZSM-22/Al₂O₃ in both conversion and isomer yield. Interestingly, the location of Pt (on Al₂O₃ or ZSM-22) had no effect on the distribution of mono-methyl isomers, indicating that this is governed mainly by the zeolite's channel structure.

Given that industrial catalysts require shaping (unlike direct loading onto pure zeolite powders in laboratory settings), Liu et al. (2016b) found that shaping ZSM-22 prior to ion exchange led to better Pt dispersion. Hydrocracking tests of tail oil showed the performance ranking: shaped-then-exchanged > direct zeolite ion exchange > incipient wetness impregnation. Under optimized conditions (pH = 9, Pt loading = 0.30 wt%), the Pt dispersion reached 87.2%, and the base oil yield reached 75.8%.

Beyond the choice of loading method, the type of metal precursor and solvent also influence Pt particle size and exposed crystal facets. Wang et al. (2015) investigated how different Pt precursors affected the catalytic performance of Pt/ZSM-22 in n -C₁₆ hydroisomerization. As shown in Fig. 7, Pt particles prepared using H₂PtCl₆ were smaller and had a higher proportion of active (111) facets, whereas Pt prepared using Pt(NH₃)₄Cl₂ had larger particle sizes with more (100) facets. Notably, Pt(111) surfaces exhibit superior hydrogenation/dehydrogenation activity compared to Pt(100). Furthermore, precursors with anionic ligands (e.g., H₂PtCl₆ and (NH₄)₂PtCl₄) produced smaller Pt particles and higher isomer selectivity than those with cationic ligands (e.g., PtCl₄ and Pt(NH₃)₄Cl₂).

Ning et al. (2018) dissolved Pt precursors in different solvents—water, ethanol, acetone, and acetic acid—and prepared a

series of Pt/ZSM-22-Al₂O₃ catalysts by impregnation. Evaluation using n -C₁₂ revealed that solvent polarity was the key factor affecting Pt dispersion. When ethanol, acetone, or acetic acid was used, Pt tended to distribute on the outer surface of ZSM-22, interacting with BAS and exhibiting electron-deficient states, which enhanced hydrogenation/dehydrogenation activity. In contrast, when water was used as the solvent, Pt was primarily distributed on the alumina, with minimal effect on its electronic properties.

Supported metal catalysts typically require pretreatment to reduce metal oxides to their active metallic states. However, conventional high-temperature H₂ reduction often leads to metal sintering, which decreases dispersion and catalytic efficiency (Beck et al., 2020; Hansen et al., 2013). Recent studies have demonstrated that room-temperature electron reduction (RTER) is a promising alternative. For example, Li et al. (2024a) applied RTER pretreatment to Pt-Pd/ZSM-22 catalysts and observed significantly higher metal dispersion and greater exposure of (111) facets compared to conventional H₂-reduced samples, thereby enhancing the hydrogenation/dehydrogenation activity toward olefin intermediates. Using this technique, their team developed Pt/ZSM-22 and Pd/ZSM-12 catalysts that achieved superior isomerization yields of n -C₆ (76.3%) and n -C₁₆ (80.2%), respectively (Li et al., 2020; Lin et al., 2022).

Overall, the preparation of bifunctional catalysts using zeolites as supports requires careful consideration of the metal loading method, precursor type, and pretreatment conditions. The studies discussed above demonstrate that even at constant noble metal loadings, optimizing metal deposition and pretreatment can significantly improve the performance of ZSM-22-based catalysts—such as by selectively localizing metal on alumina binders rather than within the zeolite channels, minimizing particle size, increasing dispersion, and exposing desirable crystal facets. However, most of these efforts have focused on enhancing hydrogenation/dehydrogenation activity, with limited attention given to sintering resistance. It is important to note that noble metal sintering under reaction conditions can substantially accelerate catalyst deactivation (Loria et al., 2011; Goodman et al., 2017). Therefore, strategies to optimize metal function must also account for the thermal stability and sintering resistance of noble metal sites.

4.2. Development of non-noble metals

Although noble metals such as Pt and Pd are typically used in low loadings (usually ≤0.5 wt%), their high cost remains a major barrier to large-scale industrial application. Research has shown that non-noble metals such as Ni and Co are promising alternatives, but suppressing undesired hydrocracking side reactions is the primary challenge (Ding et al., 2015; Srifa et al., 2015). To address this, tuning the metal loading and constructing bimetallic active sites have emerged as direct strategies for optimizing metal functionality.

The loading amount of non-noble metals not only affects the molar ratio of metal to acid sites but also determines the distribution of active species. For example, Zhang et al. (2024c) synthesized Ni/ZSM-22 catalysts with varying Ni contents using defect-engineered ZSM-22 and evaluated them for n -C₁₂ hydroisomerization. XRD analysis revealed that when the Ni loading was below 2.0 wt%, the catalyst primarily formed type I NiO_x species—unsaturated-coordination NiO_x strongly interacting with the support. When the loading exceeded 2.0 wt%, type II NiO_x species resembling bulk NiO were formed, which interacted weakly with the support. Therefore, suppressing the formation of type II NiO_x while promoting type I NiO_x is critical for high-

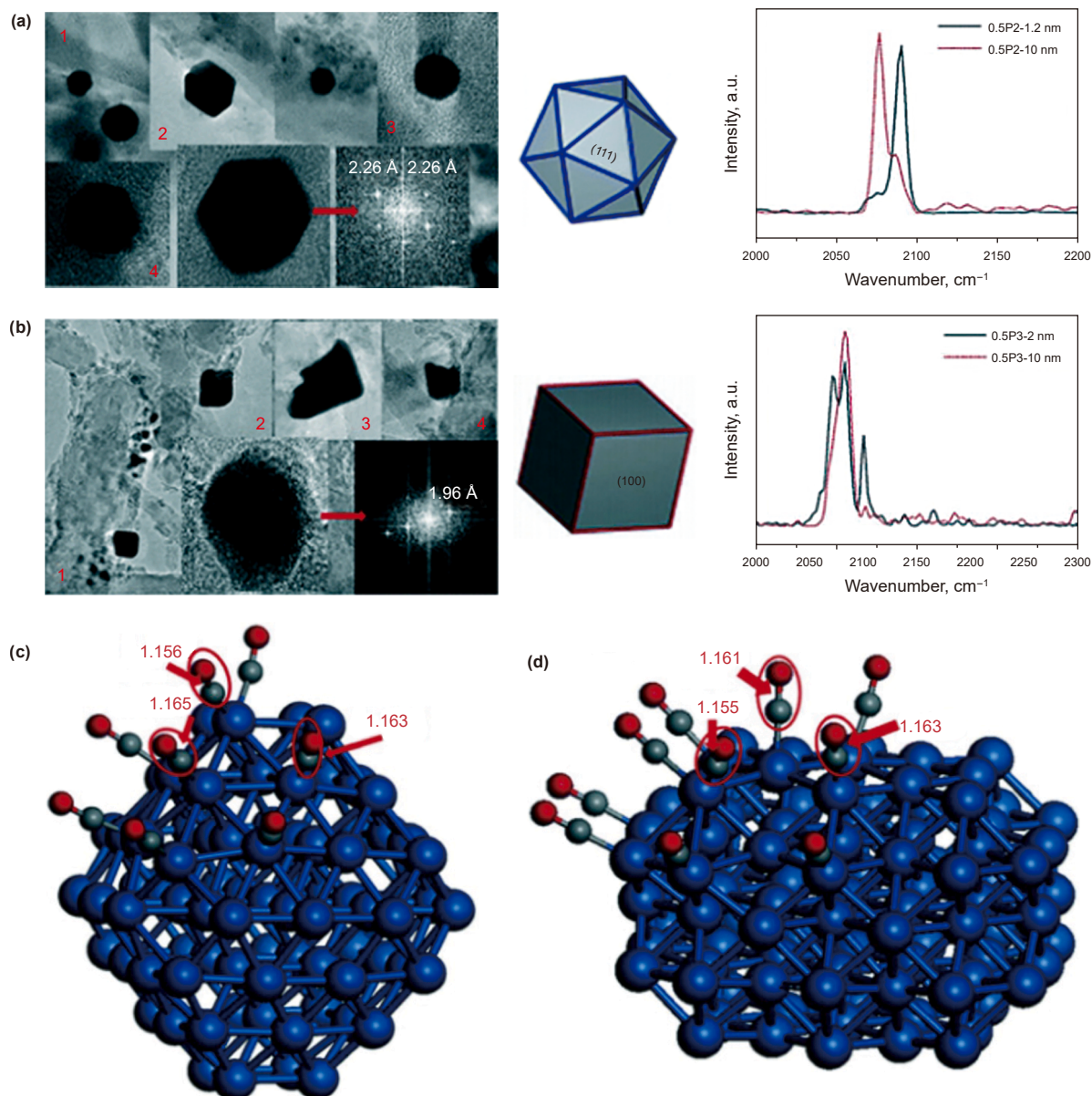


Fig. 7. HRTEM images and CO-IR spectra of Pt/ZSM-22 catalysts with 1.2 and 10 nm particle size: (a) Pt particles reduced from H_2PtCl_6 precursor and (b) Pt particles reduced from $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ precursor, and calculated CO adsorption on the model of (c) Pt (111) facet and (d) Pt (100) facet. Adapted from ref (Wang et al., 2015) with permission from Elsevier.

performance Ni/ZSM-22 catalysts. Based on this insight, the group tailored ZSM-22 morphology—preparing nano- and fibrous-bundle ZSM-22—to strengthen Ni-support interactions, thereby significantly enhancing isomerization performance (Zhang et al., 2023, 2024b). Similarly, Liu et al. (2018) studied the effect of Co loading on ZSM-22 for the deoxygenative isomerization of palmitic acid, finding that 4 wt% Co achieved an isomer yield of 73.4%. Further improving the mesoporosity of ZSM-22 increased the yield to 76.5% and improved catalyst stability (Cao et al., 2018). These studies confirm that tuning metal loading to optimize the distribution of non-noble species is an effective strategy to suppress hydrocracking.

Compared to single-metal systems, bimetallic active sites—through strong interactions between two metal components—can achieve specific geometries (e.g., alloy, core-shell, or phase-separated structures) and modified electronic properties, thereby improving catalytic performance (Jao et al., 1996;

Mériaudeau et al., 2005). To date, studies on bimetallic systems supported on ZSM-22 for long-chain alkane isomerization are limited. Therefore, Y (3D), β (3D), ZSM-23 (1D), and SAPO-11 (1D) zeolite-based catalysts are used here as illustrative examples.

Due to similar valence electron configurations, Ni can easily form bimetallic sites with Pd or Pt via chemical or electrochemical methods. Karthikeyan et al. (2008) prepared Pd-Ni/Y catalysts containing 0.1 wt% Pd and 0.1–0.5 wt% Ni for *n*-C₈ hydroisomerization. Introducing Ni significantly reduced the reduction temperature of Pd, attributed to enhanced interaction between Ni species and reduced Pd particles, which increased hydrogen chemisorption. In addition, Pd-Ni ion-pair formation or Ni migration improved Pd reducibility. The Pd-Ni bimetallic particles also exhibited better dispersion than monometallic Pd, covering more BAS and optimizing the metal-acid balance. As a result, Pd-Ni/Y achieved a higher isomer yield (90%) compared to Pd/Y (83%) and Ni/Y (54%).

Beyond elemental Ni, Ni₂P and its analogs can also form bimetallic systems with noble metals, offering even stronger hydrogenation/dehydrogenation capacity. Yao et al. (2015) synthesized Ni₂P/ β via hydrothermal methods, then introduced trace amounts of Pt (0.05 or 0.1 wt%) to form bimetallic catalysts. For isomerization of *n*-C₇, Pt_{0.1%}/ β and Ni₂P_{30%}/ β exhibited poor yields (5.4% and 11.7%, respectively), due to the low Pt loading and insufficient activity of Ni₂P. In contrast, the bimetallic Pt_{0.1%}-Ni₂P_{30%}/ β catalyst delivered a markedly higher yield of 51.1%.

Thanks to their cost advantages, non-noble bimetallic catalysts have attracted considerable attention. For instance, in the Ni_{2.0%}Cr_{2.0%}/ZSM-23 catalyst prepared by Wang et al. (2024b), the close contact between CrO_x and Ni promotes the formation of small Ni nanoparticles and increases their electron density, leading to a higher *i*-C₁₆ yield (82.9%) than that of the Pt-based catalyst (78.9%). In a study on SAPO-11-supported systems, Dai et al. (2022) introduced secondary metals such as La, Ga, Ce, and Zr to prepare Ni_{4.0%}Me_{2.0%}/SAPO-11 catalysts. They found that NiGa/SAPO-11 achieved an *i*-C₁₆ yield of 64.90%, close to that of Pt/SAPO-11 (68.80%). Similarly, work on Ni_{3.0%}Cu_{1.5%}/SAPO-11 has also proven that the Ni-Cu bimetallic system can effectively suppress hydrogenolysis, raising the isomerization selectivity of *n*-C₈ to 95% at 70% conversion compared to its monometallic Ni counterpart (Yang et al., 2017).

A broader review of the literature reveals that several non-noble bimetallic catalysts such as Ni-Co/ZSM-5, Ni-H₃PW₁₂O₄/SiO₂, Ni-W/ZrO₂, and Ni-Mo/SAPO-11 can achieve performance comparable to noble metal systems (Qiu et al., 2008; Sakashita et al., 2011; Wang et al., 2020a). However, most of these studies focus on hydroisomerization of light alkanes, and their applicability to long-chain alkanes remains unclear. Additionally, variations in metal-support interactions may limit the reproducibility of metal functionality on ZSM-22. Aljajan et al. (2023) further pointed out that the hydrogenation/dehydrogenation performance of bimetallic sites varies with alkane chain length. Therefore, further investigation is needed to develop effective strategies for optimizing non-noble bimetallic catalysts supported on ZSM-22.

5. Functional modification strategies for ZSM-22

It is worth noting that simply enhancing metal functionality is often insufficient to address the challenges faced by zeolite-based catalysts under harsh industrial conditions, such as poor resistance to coke formation and difficulty in regeneration. As a result, many studies have suggested that developing functionally modified zeolites is a mainstream strategy for improving the hydroisomerization performance of alkane catalysts. In the case of ZSM-22, approaches such as synthesizing nanosized crystals and constructing hierarchical pore structures can help alleviate the diffusion limitations imposed by its narrow channels on alkanes and olefin intermediates. Additionally, to address the issue of strong BAS typically arising from framework aluminum in ZSM-22, strategies including framework heteroatom substitution, ion exchange, and selective passivation of BAS have been proposed as potential solutions.

5.1. Synthesis of nanosized zeolites

The extended microporous channels of ZSM-22 can increase the likelihood of side reactions. To enhance exposure of the pore mouths, the most direct strategy is to reduce the crystal size of the zeolite. Over the past two decades, researchers have developed various methods for synthesizing nanosized zeolites, including supersaturation-driven synthesis, low-temperature template-free methods, and seed-assisted crystallization (Chen et al., 2024).

However, most of these approaches are difficult to generalize to 1D-10 MR zeolites such as ZSM-22 or ZSM-23, due to the challenge of controlling crystal growth along their preferential orientation parallel to the channels (Feng et al., 2019). Currently, the two mainstream methods for synthesizing nanosized ZSM-22 are template-directed synthesis and growth inhibitor approaches.

Templates typically consist of alkali metal cations or positively charged organic molecules. Their structure, size, and dosage significantly influence the supersaturation of the system, the number of nucleation sites, and the nucleation rate. Based on this principle, our team proposed a method to tune ZSM-22 crystal size by adjusting the alkyl chain length of the structure-directing agent (Wang et al., 2023b). As shown in Fig. 8, extending the carbon chain length of the template (C₂N₂(CH₂)_{*n*}, where *n* = 4, 6, 8, 10) enabled the control of ZSM-22 crystal size from the microscale (13 μ m $\times$ 1.71 μ m) to the nanoscale (250 nm $\times$ 44 nm). Crystallization mechanism studies revealed that long-chain templates promote nucleation of aluminosilicate species, and that the independent growth of initial nanorods suppresses their fusion into larger crystals. In *n*-C₁₆ isomerization reactions, nanosized ZSM-22 demonstrated superior isomerization performance (with yields exceeding 70%) and excellent catalytic stability. Moreover, the isomer products were enriched in multi-branched isomers and mono-branched isomers with methyl groups located near the center of the carbon chain.

However, it is important to note that the effectiveness of using templates to control crystal size is significantly influenced by other synthesis conditions, such as precursor composition and hydrothermal parameters. For example, Zhang et al. (2024a) synthesized ZSM-22 using diethylamine and 1,6-hexanediamine as structure-directing agents. Their results showed that while the template structure affected the morphology and aggregation state of the zeolite, it had only a minor effect on the actual crystal size. Similarly, Zhang et al. (2012) employed 1,6-hexanediamine and 1-ethylpyridinium bromide as templates and obtained ZSM-22 crystals with rod-like and plate-like morphologies, respectively. However, the differences in average length and width between the two samples were both under 5%.

In contrast to conventional organic templates, ionic liquids have shown great potential in zeolite synthesis due to their unique physicochemical properties, such as high thermal stability, low vapor pressure, and tunable cation–anion structures (Wen et al., 2014; Lu et al., 2016; Li et al., 2021). For instance, Song et al. (2025b) used 1-butyl-3-methylimidazolium chloride as a template to synthesize nanosized ZSM-22 at 180 °C, achieving crystals with lengths of 800–1000 nm and diameters of 50–80 nm. In the hydroisomerization of *n*-C₁₂, the authors attributed the superior isomer yield (~72%)—compared to ~54% for large-crystal samples—to the higher crystallinity and lower concentration of Si-OH defect sites in the nanosized zeolite. Beyond monomethylimidazolium-based ionic liquids, di- and trimethylimidazolium variants have also shown promise in ZSM-22 synthesis (Lopes et al., 2015; Vinaches et al., 2017). In addition, some researchers have developed a new synthesis method using ionic liquids as reaction media—known as ionothermal synthesis (Vinaches and Pergher, 2019). Compared to conventional hydrothermal synthesis, ionothermal methods can operate near atmospheric pressure. However, the relatively high cost and potential toxicity of certain ionic liquids remain key limitations to their widespread adoption.

As shown in Fig. 9, Hayasaka et al. (2007) synthesized ZSM-22 using 1,6-hexanediamine as a template at 150 °C, and characterized products obtained at different crystallization times to elucidate the crystal growth mechanism. Their study revealed that nanosized ZSM-22 crystals predominantly formed during the early

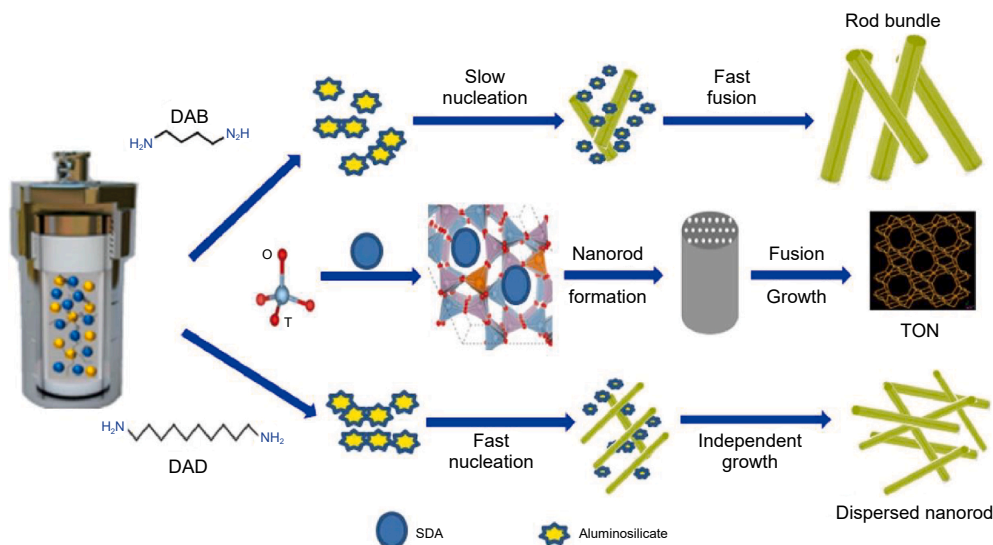


Fig. 8. Proposed evolution process for ZSM-22 with in 1,4-butanedi-amine (DAB) and 1,10-decanedi-amine (DAD) systems. Adapted from Wang et al. (2023b) with permission from ACS.

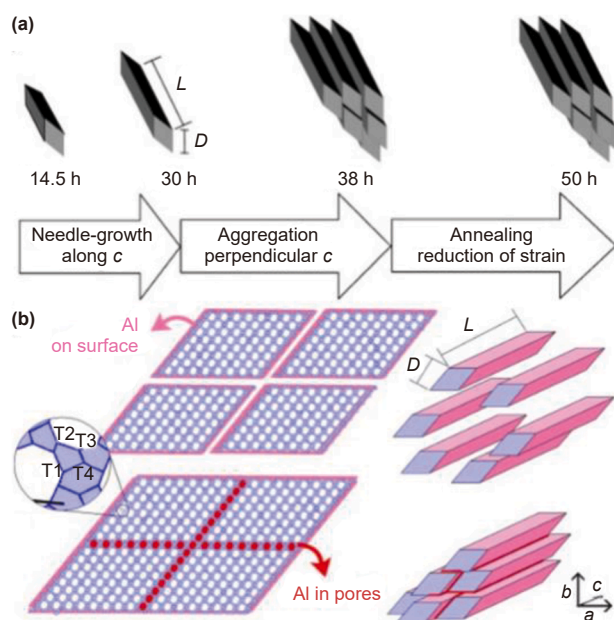


Fig. 9. Evolution mechanism of ZSM-22: (a) crystal growth behavior and (b) nanorod aggregation model. Adapted from Hayasaka et al., (2007) with permission from Wiley.

stage of synthesis (within 24 h), appearing as isolated nanorods with cross-sectional lengths of approximately 12 ± 4 nm. In the later stages of crystallization, these nanorods underwent lateral alignment and fusion, resulting in crystal growth. Building upon these findings, a series of growth-inhibitor strategies have since been proposed for the preparation of nanosized ZSM-22, where the choice of growth inhibitor plays a crucial role in controlling crystallite size.

Unlike templates, growth inhibitors do not participate in the hydrolysis or nucleation processes of the zeolite gel. Their sole function is to restrict the growth and aggregation of primary nanocrystals (Wen et al., 2014). Okamoto et al. (2018) demonstrated that when fluorides are used as mineralizing agents in

ZSM-22 synthesis, nonionic surfactants such as $C_{16}EO_{10}$ are particularly effective in reducing crystal size. When hydroxides are used instead, bulky amines—such as poly(ethylene oxide)—can serve as growth inhibitors. Microscopic observations confirmed that growth inhibitors adsorb onto the pore mouths of initial ZSM-22 nanorods, thereby suppressing axial growth along the channel direction. In n -C₁₄ hydroisomerization tests, the resulting nanosized ZSM-22 exhibited an improved isomer yield of 75%.

Zhang et al. (2021) synthesized nanosized ZSM-22 (~310 nm) using a cationic copolymer containing quaternary ammonium groups (COPQA) as a growth inhibitor. Compared to ZSM-22 synthesized without COPQA, the nanosized version exhibited significantly higher isomer selectivity (93.5%) at a similar n -C₁₂ conversion (~90%). Urea has also been used as a growth inhibitor to prepare layered ZSM-22 structures. However, these platelets tend to aggregate along the channel direction, leading to elongated diffusion paths within the crystals and reduced accessibility for alkanes and intermediates (Liu et al., 2023a).

In addition to template-directed and growth-inhibitor strategies, some researchers have reduced ZSM-22 crystal size through multidimensional control of synthesis conditions or by introducing physical assistance. However, these methods are relatively complex and less suitable for large-scale production. For example, Han et al. (2022) synthesized ZSM-22 with particle sizes ranging from 100 to 330 nm by employing a combination of low-temperature aging, seed addition, and increased synthesis alkalinity. The resulting Pt/ZSM-22 catalyst achieved a jatropa oil conversion rate of 97.79%, with a bio-jet fuel yield of 50.25%. Zhai et al. (2022) prepared ZSM-22 with crystal sizes between 100 and 300 nm using mechanical bead milling followed by recrystallization. Catalytic tests with n -C₇ revealed that for ZSM-22 with Si/Al = 200, the isomer yield increased from 56% (in the parent zeolite) to 74% after nanosizing.

5.2. Design of hierarchical pore structures

In addition to reducing crystal size, constructing hierarchical pore structures is also an effective strategy to mitigate the diffusion limitations of ZSM-22's microporous channels. On the one hand, hierarchical porosity significantly increases the number of pore mouths and the density of BAS at these mouths, allowing

alkanes to isomerize more readily at the external surface. On the other hand, shortening the effective micropore length reduces the residence time of alkanes within the channels, thereby lowering the likelihood of undesired cracking. In recent years, two main approaches have been used to prepare hierarchical ZSM-22: top-down and bottom-up methods (Li et al., 2018).

The top-down method, also known as post-treatment, introduces mesopores by secondary treatment of the zeolite. A widely adopted technique is the selective removal of silicon or aluminum from the framework to generate intracrystalline voids (Valtchev et al., 2008; Ba et al., 2018). However, in the case of ZSM-22—which contains much less framework aluminum than silicon—dealumination is less applicable. Desilication, by contrast, is more commonly used and typically involves alkaline solutions such as NaOH, NaAlO₂, Na₂CO₃, or TPAOH (He et al., 2021). Wu et al. (2018) found that increasing NaOH concentration reduces both the total acidity and BAS density of ZSM-22, while preserving the crystal structure and micropore architecture in low-Si/Al samples. Compared with the parent ZSM-22, alkali-treated samples exhibited improved *i*-C₁₂ selectivity (from 59.5% to 87.3%) and yield (from 43.3% to 69.8%).

However, alkali treatment may lead to the redeposition of extracted silicon species, blocking mesopores and micropores and reducing acidity. It has been shown that subsequent acid washing can remove these deposits and restore pore connectivity. Martens and co-workers (Martens et al., 2013a, 2013b) found that during desilication, nanorod-like ZSM-22 crystals were physically separated, forming interstitial mesopores. Mild acid washing then removed obstructive aluminum species near the pore mouths and effectively reorganized the spatial distribution of BAS. Compared to the parent zeolite, the treated samples had fewer microporous BAS but more BAS at the pore mouths. *n*-Decane and *n*-nonadecane testing showed that the treated ZSM-22 achieved ~35% (*n*-C₁₀) and ~42% (*n*-C₁₉) yields of multi-branched isomers. Guo et al. (2022) further treated alkali-treated ZSM-22 with hydrochloric acid solutions of fluorosilicic acid (H₂SiF₆), achieving a multi-branched *i*-C₇ yield of 13.6%—four times that of untreated ZSM-22.

Different alkaline solutions result in different desilication mechanisms. NaOH-treated catalysts, for instance, tend to experience aggressive surface erosion by OH[−] ions, which significantly reduces crystal size without altering the micropore structure. To control pore architecture more precisely, template-protected alkaline treatment has been developed. Wang's group (Wang et al., 2019b) introduced a dual-template strategy combining alkaline treatment with carbonized internal templates (1,6-hexanediamine) and external surfactants (CTAB) to create uniform 3.2 nm mesopores in ZSM-22. As shown in Fig. 10, the cooperative effect of carbonized internal templates and CTAB helps direct OH[−] attack through a “drilling” mechanism, forming uniform mesopores. Compared with samples treated using alkali alone (*i*-C₁₂ yield: 54%), the hierarchical ZSM-22 achieved an improved *i*-C₁₂ yield of 73.4%.

Liu et al. (2022) prepared ZSM-22 samples with intracrystalline mesopores of 2.9, 4.3, and 9.3 nm using a combination of alkaline treatment, CTAB protection, and acid washing. Compared with untreated samples (~40% *i*-C₁₂ yield), the sample with 4.3 nm mesopores showed significantly improved *i*-C₁₂ yield (~72%) and multi-branched isomer selectivity (~25%). In addition to CTAB, other agents such as polydopamine and tetramethylammonium hydroxide have also been used as protective templates in ZSM-22 alkali treatments (Liu et al., 2025).

In summary, the core mechanism of the top-down strategy lies in the selective removal of framework elements to generate mesoporosity. By introducing additional mesopores and increasing the

density of BAS at the pore mouths, this approach effectively alleviates the diffusion limitations inherent to ZSM-22's microporous structure. However, conventional alkali treatment inevitably results in partial structural degradation and reduced crystallinity during framework etching. Therefore, optimizing top-down strategies to improve the structural stability of hierarchical zeolites is of vital importance.

The bottom-up approach introduces mesoporosity directly during the crystallization process. Among these, template-directed methods are the most widely applied and can be categorized into hard-template and soft-template methods. In hard-templating, the template must remain inert and not react with the synthesis gel components, serving only to block or confine zeolite growth. The hard template is subsequently removed by high-temperature calcination. Common hard templates include organic polymers, metal oxides, and inorganic carbon, with carbon templates being the most widely used due to their ease of removal by combustion (Jacobsen et al., 2000; Schmidt et al., 2001; Tao et al., 2003). However, this method has been mainly applied to 3D zeolites (e.g., ZSM-5, Beta, Silicalite-1, LTA), and has seen limited use for 1D-10 MR zeolites like ZSM-22. This is likely due to the highly anisotropic crystal growth and unidirectional channel system of the latter, which makes uniform growth control in all directions difficult.

The soft-templating approach uses amphiphilic molecules as mesopore templates, which participate in the hydrolysis and nucleation of the zeolite, enabling the direct construction of hierarchical structures. For example, Xiong et al. (2024) used polyhexamethylene biguanide (PHMB) to replace the conventional 1,6-hexanediamine template in the synthesis of mesoporous-rich ZSM-22. Experiments confirmed that the introduction of an appropriate amount of PHMB increased the mesopore volume (0.667 vs. 0.428 cm³/g), and the ratio of T1+T2+T3 acid sites was significantly lower than that of microporous ZSM-22 (0.652 vs. 1.000). The optimized catalyst achieved an *i*-C₁₆ yield of 76.6% and remained stable over 100 h of reaction. Similarly, Li et al. (2019a) synthesized ZSM-22 with a mesopore volume of 0.38 cm³/g and external surface area of 127 m²/g using Al₂(SO₄)₃·18H₂O as the aluminum source, silica sol as the silicon source, and organosilicon quaternary ammonium salts as the mesopore-directing agent via hydrothermal crystallization. The abundant mesoporous structure promoted better molecular diffusion and enhanced Pt dispersion, resulting in an *i*-C₁₂ yield of 73%.

Traditional soft templates typically include inexpensive and commercially available surfactants such as CTAB, di/trime-thylhexadecylammonium salts, tetrapropylammonium, and amino acids (Chen et al., 2020; Liu et al., 2025). In recent years, new templates—such as non-surfactant polymers and cationic polymers—have been developed (Wang and Pinnavaia, 2006; Xiao et al., 2006; Choi et al., 2009). However, they are often difficult to synthesize and prohibitively expensive. While the soft-template approach offers good reproducibility and adjustable Si/Al ratios, it also has certain limitations—such as high synthesis cost, poor pore connectivity, and uneven mesopore distribution.

5.3. Synthesis of heteroatom-substituted zeolites

Compared with cracking reactions, hydroisomerization of alkanes involves only carbon chain rearrangement. It has a relatively lower activation energy and therefore requires a lower acid strength than cracking. In the case of ZSM-22 zeolites, the framework aluminum typically generates strong BAS, which can intensify cracking and reduce isomerization yields. Replacing framework T atoms with other metal atoms is an effective strategy

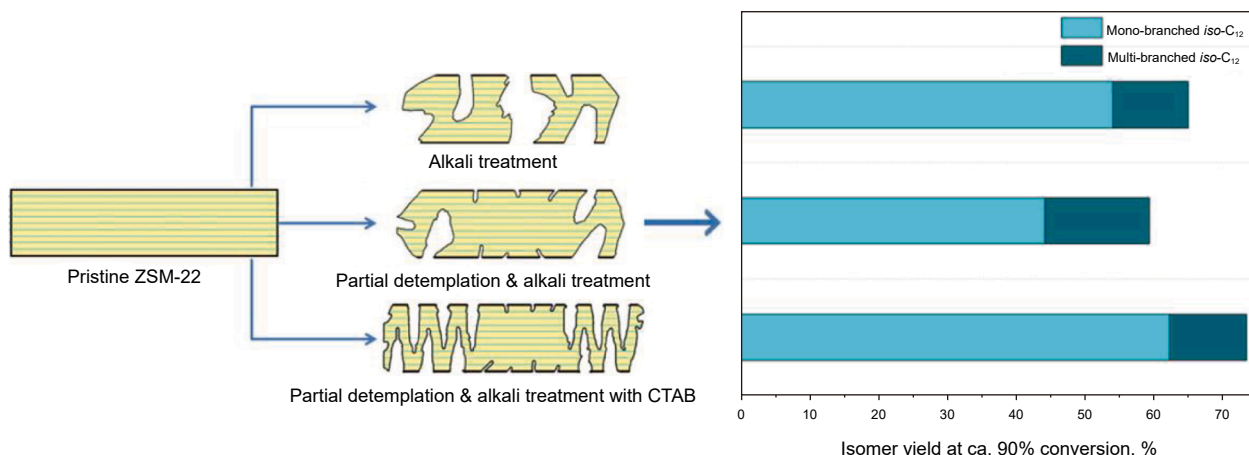


Fig. 10. Brief mechanism scheme of ZSM-22 dual-protected alkali treatment. Adapted from Wang et al. (2019b) with permission from ACS.

to tune both the zeolite framework composition and acidity (Wu et al., 2010; Zhou et al., 2015; Chen et al., 2018; Li et al., 2019b).

Liu et al. (2015) successfully synthesized a series of Fe-doped ZSM-22 zeolites (Fe content: 0–2.55 wt%) via a precursor-induced hydrothermal method by gradually replacing $\text{Al}_2(\text{SO}_4)_3$ with $\text{Fe}(\text{NO}_3)_3$. UV-vis, FT-IR, and XPS analyses confirmed the incorporation of Fe atoms into the zeolite framework. Compared with undoped samples, the BAS strength in Fe-doped ZSM-22 decreased with increasing Fe content, due to the lower polarizability of Fe compared to Al. As a result, the Fe–OH–Si bridging hydroxyls exhibited weaker acidity than the conventional Al–OH–Si bridges. Additionally, small amounts of Fe^{3+} also acted as nucleation promoters during synthesis, producing ZSM-22 with smaller crystal sizes. In n -C₁₂ hydroisomerization, the Fe-doped sample achieved a significantly higher isomerization yield (~80%) compared to the undoped one (~43%). Building upon this work, the same group later synthesized Ga-doped ZSM-22 catalysts (0–2.61 wt%) and found that Ga, which offers better framework stability than Fe, also led to performance improvements (Liu et al., 2019).

In addition to Fe and Ga, main group metals have also been explored for heteroatom-doped ZSM-22 synthesis. Niu et al. (2018b) synthesized B-doped ZSM-22 zeolites with varying Si/B ratios (55, 91, 177) using a seed-assisted hydrothermal approach. Both experimental and computational studies revealed a higher proportion of weak BAS in B-doped ZSM-22, though its activation capacity for n -C₁₂ was relatively low—thus requiring higher temperatures for the reaction. Notably, the presence of weak BAS significantly increased the yield of centrally branched i -C₁₂ isomers, reaching up to 47%.

To date, most heteroatom doping efforts have focused on transition metals due to their small ionic radii, symmetric structures, and the spatially extended d-orbitals, which facilitate incorporation into zeolite frameworks (Li et al., 2024b). However, previously reported Fe, Ga, and B doping strategies do not significantly alter the pore mouth size of ZSM-22. To address this, our group synthesized a series of Ce-doped ZSM-22 zeolites (Ce content: 0–4.63 wt%) using a seed-assisted hydrothermal route (Wang et al., 2023a). BET analysis showed that as Ce content increased, the microporous surface area (207 to 9.8 m²/g), micropore volume (0.088 to 0.004 cm³/g), and average micropore diameter (0.353 to 0.465 nm) all decreased gradually. DFT simulations indicated that Ce preferentially occupies the T1 framework site, while Al prefers T2, T3, and T4 sites—suggesting a complementary distribution. Compared with Ce-free or impregnated ZSM-22 samples, Ce-doped ZSM-22 achieved isomerization yields exceeding 75%.

These studies collectively demonstrate that current heteroatom-substituted ZSM-22 syntheses often rely on seed addition or precursor design. Nonetheless, several technical challenges remain, including low framework doping levels (<5 wt%) and uncontrollable heteroatom location. These issues likely stem from:

- The metastable topology of ZSM-22, which is highly sensitive to synthesis conditions (e.g., temperature, precursor types, and composition ratios), restricting the incorporation window for heteroatoms.
- The use of strong alkaline environments, which can lead to heteroatom precipitation as hydroxides, resulting in extra-framework species or uneven distribution.
- The competitive siting mechanisms between heteroatoms and Al/Si remain poorly understood.

Thus, developing efficient and controllable heteroatom-doping strategies is essential for further enhancing the hydroisomerization performance of ZSM-22-based catalysts.

5.4. Ion exchange and selective passivation of brønsted acid sites

For ZSM-22, moderate acid strength is beneficial for improving isomerization selectivity, but it may also lead to decreased catalytic activity. Therefore, to strike a balance between activity and selectivity, tuning the acidity of ZSM-22 requires an integrated strategy that combines moderate acid strength with an adequate density of acid sites. Unlike framework-level modifications such as heteroatom substitution, ion exchange and selective passivation of BAS offer alternative and effective routes to adjust catalytic performance.

In the case of common Na- or K-type ZSM-22 zeolites, which are generally considered inactive for alkane conversion, ion exchange becomes a critical step for modulating isomerization activity. Wang et al. (2008) treated K-type ZSM-22 using ammonium nitrate, nitric acid, and ammonium hexafluorosilicate. Among the three, the sample treated with ammonium nitrate showed the highest n -C₁₂ conversion, though excessive cracking occurred due to strong acidity. The use of ammonium hexafluorosilicate led to significant dealumination and increased the framework Si/Al ratio, lowering acidity and thus reducing conversion. Notably, the sample co-treated with ammonium nitrate and ammonium hexafluorosilicate exhibited the highest proportion of medium-strength BAS, achieving 88.0% isomer selectivity at 87.5% conversion. Similar results were obtained by

Wang et al. (2011), who used ammonium hexafluorosilicate solutions of varying concentrations to selectively remove strong acid centers, thereby suppressing n -C₁₀ cracking. In another study, Guo et al. (2021) demonstrated that combining ammonium nitrate with diluted nitric acid also allows effective tuning of ZSM-22 acidity. The treated zeolite exhibited a higher proportion of medium-strength BAS and reached an isomer yield of ~80% during n -C₁₂ hydroisomerization.

It is worth noting that dealumination induced by ammonium hexafluorosilicate or dilute nitric acid can lead to partial degradation of the ZSM-22 framework. In contrast, neutral metal salt ion exchange has proven to be a milder and more structure-preserving method. Parmar et al. (2015) explored the ion exchange of ZSM-22 with alkaline earth metal cations (Mg²⁺, Ba²⁺, Ca²⁺), and found that Ca²⁺-exchanged ZSM-22 had the highest density of medium-strength BAS. This catalyst achieved a selectivity of 85.8% and an isomer yield of 77.8%, with nearly 90% of the products being mono-branched isomers. Bai et al. (2020) developed a Zn²⁺-modified ZSM-22 as the acidic component and Ni as the metallic component for hydroisomerization of Fischer-Tropsch diesel. Zn²⁺ modification reduced the Brønsted/Lewis acid site ratio, effectively suppressing cracking and improving the diesel yield to 90.65%.

In general, ion exchange-based acidity tuning involves well-defined steps, among which the choice of exchange cation is crucial. The extent of ion incorporation is strongly influenced by the parent sample's acidity, precursor solution concentration, and ion exchange temperature.

Importantly, BAS located at different positions within the ZSM-22 framework play distinct roles in alkane hydroisomerization. BAS at the pore mouth are generally considered beneficial for selective isomerization. Based on this principle, researchers have developed selective BAS passivation strategies to enhance catalytic performance (Wang et al., 2025). Common approaches include shielding external acid sites or partially blocking internal micropores.

For example, Chen et al. (2017) synthesized a ZSM-22@SiO₂ core-shell structure via epitaxial growth to selectively shield external acid sites. As shown in Fig. 11, during the hydrodeoxygenation and isomerization of methyl palmitate, increasing SiO₂ content from 0 to 20% raised mono-branched isomer selectivity from 71% to 95%. Further increase in SiO₂ loading had no additional effect, and excessive coating also reduced catalytic activity. Thus, 20% was deemed the optimal loading to balance selectivity and activity. Lv et al. (2019) prepared partially micropore-filled ZSM-22-PF supports by performing low-temperature (350 °C) template calcination. FT-IR analysis confirmed that residual coke from template decomposition remained in the micropores. This partial blockage reduced diffusion resistance and lowered the accessibility of deep-seated BAS. As a result, Pt/ZSM-22-PF showed a turnover frequency (TOF) of 314 h⁻¹—more than twice that of conventional Pt/ZSM-22 (144 h⁻¹)—and improved i -C₁₂ yield (89% vs. 83%). Theoretical simulations and adsorption studies confirmed that partial micropore filling significantly reduced diffusion limitations and shifted BAS accessibility toward the pore mouth, thereby favoring the formation of center-branched and multi-branched isomers.

To achieve the dual goal of shielding external acid sites and partially blocking internal micropores, Niu et al. (2018a) synthesized a core-shell structured ZSM-22@SiO₂ zeolite via epitaxial growth, followed by template-assisted carbon deposition to partially fill the micropores, thereby enhancing the shape-selective performance of ZSM-22. On one hand, the mesoporous silica shell not only masked the surface BAS but also facilitated the deposition and confinement of Pt nanoparticles, establishing nanometer-scale proximity between the metal and acid sites. On

the other hand, the partially blocked micropores reduced diffusion limitations and the accessibility of internal BAS. This synergistic modification significantly suppressed cracking side reactions, leading to a marked improvement in n -C₁₂ isomer yield (80.8% vs. 68.2%). Building upon this methodology, Wang et al. (2025) also demonstrated the enhancement of n -C₁₆ isomerization using a SiO₂-coated ZSM-22 followed by template carbonization. Compared to the parent zeolite, the modified ZSM-22 exhibited not only higher isomer yield (87.9% vs. 70.4%) but also superior mono-branched isomer selectivity.

These studies highlight that selective passivation of BAS serves as an effective, indirect approach for tailoring the acidity of ZSM-22. Unlike framework modifications, this strategy minimizes damage to the zeolite's crystalline structure. However, it also introduces greater complexity into catalyst preparation. Moreover, the performance of passivated ZSM-22 is strongly influenced by the intrinsic physicochemical properties of the parent zeolite, such as its Si/Al ratio, particle size, and morphology.

6. Engineering of co-crystallization and composite zeolites

Compared with direct or indirect modification approaches, constructing co-crystallization or composite structures is the most straightforward strategy for tuning the catalytic performance of ZSM-22 zeolites. The core advantage lies in overcoming the limitations of 1D pore systems while simultaneously optimizing acidity, pore architecture, and diffusion properties. However, due to the diversity of co-crystallization/composite systems, the mechanisms underlying performance enhancement are still predominantly inferred from product distribution analyses. While most improvements are attributed to synergistic effects, there remains debate over the dominant contributing factor—whether diffusion enhancement or acidic synergy. Molecular dynamics simulations and adsorption studies tend to support diffusion optimization as the primary driver, though in the case of 10-membered-ring zeolites, acid-site synergy may play a more critical role. As research on shape-selective catalysis using co-crystallization/composite zeolites continues to advance, the mechanistic understanding of hydroisomerization over these materials is expected to become increasingly clear.

6.1. Co-crystallization zeolites

The formation of co-crystallization zeolites requires structural compatibility between different zeolitic units during the crystallization process. Their catalytic performance is highly dependent on both the nature and proportion of the introduced secondary crystalline phase. Reported co-crystallization partners of ZSM-22 include mesoporous materials, 1D-10 MR zeolites, and amorphous aluminosilicates. Notably, the synthesis method plays a decisive role in controlling the composition and distribution of the eutectic phases. To date, three main strategies have been employed for the preparation of co-crystallization ZSM-22-based zeolites: alkaline desilication-recrystallization, mixed-template synthesis, and two-step crystallization.

Among these, alkaline desilication-recrystallization has emerged as a widely used method. In this approach, the parent ZSM-22 is first subjected to desilication to extract siliceous species, which are subsequently used along with the zeolite and an additional template in a secondary crystallization step to yield the target composite (Niu et al., 2005). The eutectic phases formed via this method are typically located on the external surfaces of ZSM-22, and their content can be tuned by adjusting the feed ratio during the second crystallization.

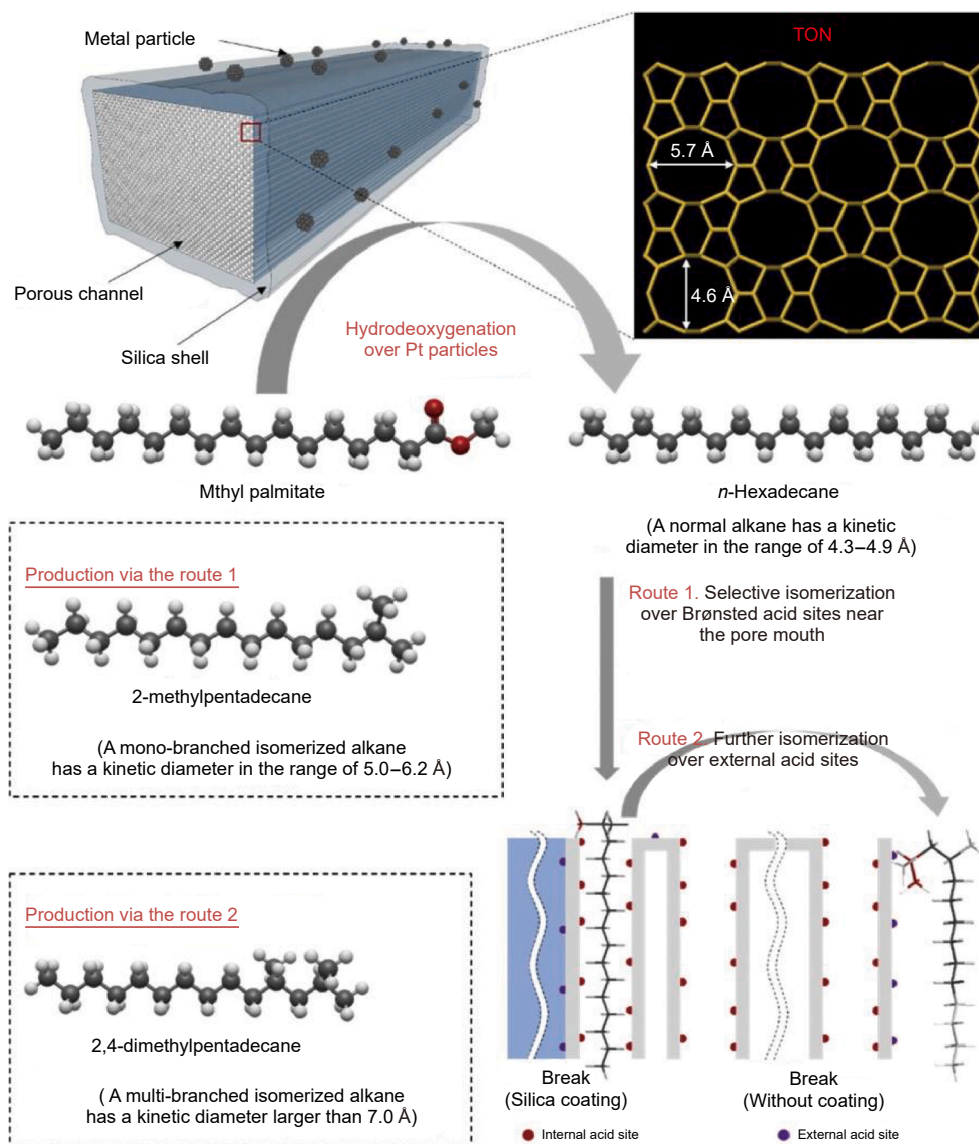


Fig. 11. Deoxygenation of methyl palmitate and further isomerization of the deoxygenated *n*-alkane into monobranched iso-alkane over Pt/ZSM-22/SiO₂. Hexadecane and the corresponding isomers are selected as examples. Adapted from [Chen et al. \(2017\)](#) with permission from Elsevier.

As shown in [Fig. 12](#), [Liu et al. \(2016a, 2020, 2022\)](#) synthesized a series of ZSM-22/MCM-41 co-crystallization zeolites via this method using cetyltrimethylammonium bromide (CTAB) as the secondary template. *n*-C₁₂ hydroisomerization tests demonstrated that the introduction of MCM-41 mesopores imparted several benefits. Firstly, the open mesoporous environment facilitated secondary skeletal rearrangements of reaction intermediates, thereby increasing the selectivity toward multi-branched isomers (18% vs. 4%). Secondly, the large surface area of MCM-41 significantly improved the metal dispersion (75% vs. 42%), which helped maintain both activity and long-term stability. As a result, the *i*-C₁₂ yield over Pt/ZSM-22/MCM-41 reached ~84%, compared to ~65% for the unmodified Pt/ZSM-22. It is important to note that the desilication-recrystallization method can reduce the intrinsic microporosity of ZSM-22, which may lower the selectivity toward mono-branched isomers. Therefore, identifying an optimal desilication condition and eutectic phase ratio is essential for maximizing overall isomerization performance.

The mixed-template approach offers a relatively simple and direct route to fabricate co-crystallization zeolites. This one-step

hydrothermal method utilizes two organic templates to co-direct the crystallization, resulting in a more uniform distribution of the eutectic phases. Owing to the structural similarity between ZSM-22 and ZSM-23, co-crystallization of these two 1D-10 MR zeolites can be achieved under suitable synthesis conditions. For instance, [Munusamy et al. \(2018\)](#) synthesized ZSM-22/23 co-crystallization zeolites (50%–60% TON) via hydrothermal crystallization using *N,N*-dimethylformamide and 1,6-hexanediamine as co-templates. Compared with Pt/ZSM-22 (70% *i*-C₁₆ yield), the Pt/ZSM-22/23 catalyst delivered an improved *i*-C₁₆ yield of ~80%. Similarly, [Song et al. \(2021\)](#) employed diethylamine and dimethylamine as dual templates and successfully synthesized ZSM-22/23 co-crystallization zeolites (40% TON). Catalytic evaluation revealed that Pt/ZSM-22/ZSM-23 exhibited a superior *i*-C₁₆ yield (78%) relative to Pt/ZSM-22 (54%), Pt/ZSM-23 (38%), and even their mechanically mixed composite (68%). The authors attributed this improvement to the shape-selective properties of the eutectic structure, which suppressed multi-branched isomers, and the synergistic presence of weak and medium BAS, which promoted the isomerization of olefin intermediates. [Chi et al. \(2013\)](#) also

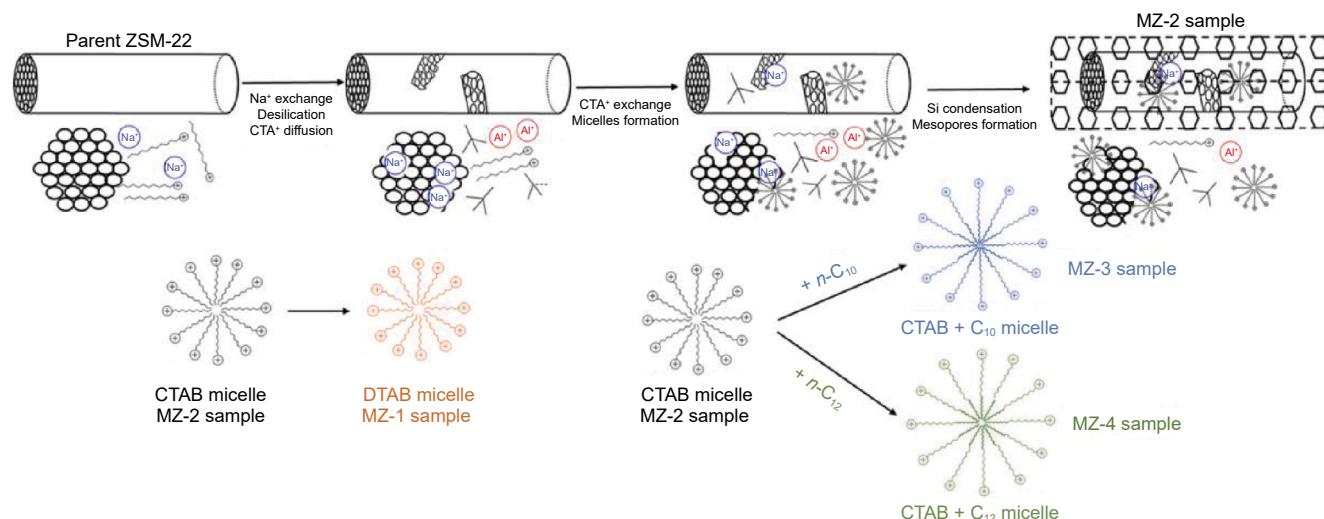


Fig. 12. Schematic representation of the hydrothermal crystallization procedure of the micro/mesoporous ZSM-22/MCM-41 samples. Adapted from Chang and Liu (2021) with permission from Elsevier.

reported a ZSM-22/23 (30% TON) co-crystallization catalyst achieving 68.3% *i*-C₁₂ isomer yield and 47% multi-branched isomer selectivity, although the overall conversion was slightly lower than for monolithic ZSM-22 or ZSM-23 catalysts.

The two-step crystallization method involves the pre-synthesis of seed crystals followed by controlled crystallization to tailor the type and proportion of eutectic phases. Key factors affecting the outcome include seed amount, morphology, size distribution, and surface defects. Wang et al. (2022) used this method to synthesize a ZSM-22/ASA co-crystallization zeolite with an ASA content approaching 90%. Characterization confirmed strong interfacial interactions between ZSM-22 and ASA, evidenced by the formation of Si-O-Al linkages. In *n*-C₁₂ isomerization tests, ZSM-22/ASA outperformed parent ZSM-22 in both isomer yield (79.4% vs. 74.2%) and multi-branched isomer selectivity (35.8% vs. 33.3%). In a related study, Wang et al. (2023c) added varying mass fractions of ZSM-22 seed crystals to the SAPO-11 synthesis gel to prepare ZSM-22/SAPO-11 co-crystallization zeolites for *n*-C₁₀ isomerization. Results showed that increasing the ZSM-22 content from 6.5% to 12.2% reduced crystal size (from 290/560 nm to 180/470 nm) and significantly enhanced medium-strength BAS content (from 15.2 to 28.4 μmol/g). Pt/ZSM-22/SAPO-11 achieved an isomer yield of 81.6%, outperforming individual SAPO-11 (~70%), ZSM-22 (50%), and their physical mixture (68%), though the isomer distribution remained largely unchanged.

These studies collectively demonstrate that co-crystallization synthesis can effectively balance acid-diffusion interactions by introducing secondary phases into the ZSM-22 framework. However, conventional alkaline desilication-recrystallization may compromise the structural integrity of the zeolite, necessitating further improvements to enhance the stability of the resulting co-crystallization systems. Additionally, due to cost concerns, the mixed-template method may not be viable for large-scale fabrication of bifunctional catalysts. In contrast, the two-step crystallization strategy holds greater potential for scalable synthesis of ZSM-22-based co-crystallization zeolites in industrial applications.

6.2. Composite zeolites

Compared to co-crystallization zeolites, which suffer from high synthesis costs and limited types of eutectic phases, the composite strategy is relatively simple and feasible, allowing for broad

regulation of diffusion and acidity, with greater tunability in enriching target products (Parton et al., 1991; Martens et al., 1993). The composites of ZSM-22 include two approaches: direct physical mixing and tandem configuration. The advantages of the composite strategy lie in high reproducibility and stability, as well as relatively simple preparation procedures. In addition, the distribution ratio of the composite zeolites is a key factor affecting catalytic performance.

Physical mixing is the most commonly used method to construct composite zeolites and is typically achieved through grinding, ball milling, or mechanical stirring (Mendes et al., 2017; Jiao et al., 2018). Xiang et al. (2024) prepared a series of MOR and ZSM-22 composite zeolites via physical mixing. The results showed that changing the relative content of MOR effectively regulated the distribution of *n*-C₁₂ isomerization products. As the MOR ratio increased from 1/9, 3/7 to 5/5, the selectivity ratio of mono-branched to multi-branched isomers at 280 °C decreased sequentially to 37.64, 15.04, 5.48, and 5.20, respectively. This showed a good complementarity with Pt/ZSM-22 (37.64) and Pt/MOR (1.47). Zero length column diffusion experiments confirmed that the low isomer selectivity of MOR was due to its poor diffusion, while ZSM-22 facilitated reactant diffusion and exhibited better catalytic performance.

Choudhury et al. (2010) evaluated the synergistic effect of physically mixed Pt/Y and Pt/ZSM-22 catalysts in the hydroconversion of *n*-C₁₀ using the SEMK model. The simulation results showed that the highest isomer yield was due to the synergy between mono-branched isomer formation on Pt/ZSM-22 and multi-branched isomer formation on Pt/Y. To achieve optimal synergy, the protonation enthalpy of carbenium ions on ZSM-22 should be at least 10 kJ·mol⁻¹ lower than on Y. Liu et al. (2023b) experimentally verified the findings of I. Roy Choudhury et al. by preparing four catalysts: Pt/ZSM-22, Pt/Y, Pt/ZSM-22 + Y (mechanically mixed ZSM-22 and Y at 1:1 wt ratio), and Pt/ZSM-22-Y (carrier treated with NaOH + CTAB). In the hydroisomerization of *n*-C₁₂, Pt/ZSM-22-Y showed the highest isomer yield (~86%) and significantly improved the yield of multi-branched isomers (37%). This may be attributed to the increased number of medium-strength acid sites and mesopores in the treated ZSM-22-Y. Based on the SEMK model, Choudhury's group conducted a series of studies on the hydroisomerization and cracking of alkanes using mixed zeolite-based catalysts (Thybaut et al., 2009; Vandegheuchte et al., 2015).

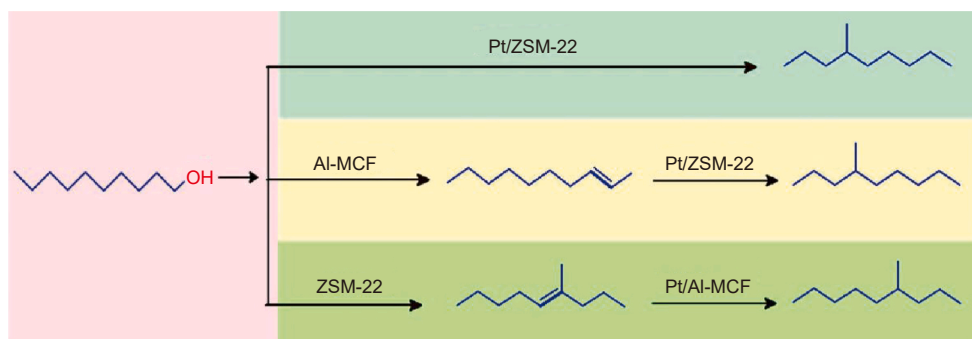


Fig. 13. Flexible catalytic process of *n*-decanol to iso-paraffin. Adapted from He et al. (2018) with permission from Elsevier.

In addition to direct physical mixing of zeolites, tandem configuration is another effective way to utilize the advantages of composite zeolites (Cheng et al., 2018; Zhang et al., 2019). Tandem configurations can be formed by arranging different zeolites or zeolites of the same type with different properties. By using the product of the upper catalyst bed as the feedstock for the lower one, tandem catalysts are widely used in the enrichment of target products. He et al. (2018) investigated the production of jet fuel through the dehydration and isomerization of *n*-decanol. As shown in Fig. 13, three different processes were tested: one-step dehydration and isomerization over Pt/ZSM-22, dehydration (Al-MCF) followed by isomerization (Pt/ZSM-22), and dehydration (ZSM-22) followed by hydrogenation (Pt/MCF). Among them, the Al-MCF/Pt/ZSM-22 process achieved the highest isomer yield (82%), and the product obtained in a pilot-scale reactor had a freezing point below -60°C , meeting all ASTM 7566 specifications except density. Jaroszewska et al. (2020) found that the synergistic effect of moderate acidity from AISBA-15 and the shape selectivity of ZSM-22 enabled the tandem catalyst composed of Pt/AISBA-15 (32%) and Pt/ZSM-22 (~42%) to achieve a mono-branched isomer selectivity of up to 67% at ~90% conversion of *n*-C₁₆. Li et al. (2022) prepared two types of ZSM-22 zeolites (L-ZSM-22, Me-ZSM-22) using L-tartaric acid and alkali treatment, respectively. In jet fuel production via hydroprocessing of *n*-C₁₆, it was found that the tandem catalyst could optimize product distribution and improve product yield. Compared with using either catalyst alone, the tandem system combined the ability of Pt/L-ZSM-22 to generate heavier alkanes and the stronger isomerization performance of Pt/Me-ZSM-22, achieving ~90% isomer selectivity at 93% conversion.

The studies presented in this section demonstrate that regulating the hydroisomerization of long-chain alkanes over ZSM-22 through physical mixing and tandem configurations is effective. However, the improvement in isomerization performance is mainly reflected in the increased selectivity toward multi-branched isomers. This may be due to the inherently higher selectivity of ZSM-22 for mono-branched isomers, while the composite components are mostly large-pore zeolites, resulting in only limited enhancement in mono-branched selectivity. Considering that multi-branched isomers are more prone to cracking, this poses a challenge to the long-term stability of the catalyst. Therefore, further optimization of composite zeolites is necessary to improve the catalyst's resistance to coking.

7. Conclusion and outlook

Hydroisomerization of *n*-alkanes over bifunctional zeolite-based catalysts is a typical BAS-catalyzed reaction with spatial confinement effects. ZSM-22, with its 1D-10 MR pore structure and tunable acidity, is among the most effective supports. To

enhance catalytic performance, the most common strategies involve optimizing the hydrogenation/dehydrogenation function of the metal and functionalizing the zeolite support. It has been demonstrated that improving metal dispersion, controlling metal deposition location, and regulating crystal facet exposure are effective approaches for enhancing metal functionality. The functionalization of ZSM-22 focuses primarily on improving molecular diffusion and tuning acidity. On the one hand, synthesizing nanosized zeolites or constructing hierarchical pore structures can alleviate the micropore diffusion resistance of alkanes and olefin intermediates, thereby reducing the likelihood of cracking. On the other hand, acidity modulation through framework heteroatom substitution, ion exchange, selective external acid site passivation, and partial pore blockage can suppress the cracking of olefin intermediates. This is because the BAS strength required for skeletal isomerization of olefins is relatively moderate, and both the external surface and internal micropores of ZSM-22 are favorable for β -scission of olefins. In addition to metal optimization and zeolite functionalization, co-crystallization and composite strategies have also proven effective in improving the catalytic performance of ZSM-22.

However, further development of ZSM-22-based bifunctional catalysts still faces several unresolved challenges. Organic structure-directing agents such as 1,6-hexanediamine, ethylenediamine, ethylpyridinium bromide, and imidazolium-based dications are commonly used in ZSM-22 synthesis. While they aid structural formation, these templates increase cost and pose environmental concerns. Developing greener and more economical synthesis routes is therefore critical for industrial application. Structurally, ZSM-22 predominantly exhibits rod-like morphology. Although various methods can significantly reduce crystal size, nanoscale ZSM-22 still shows (001) orientation dominance and non-negligible micropore diffusion limitations. Further efforts are needed to fabricate nanosheet ZSM-22 with exposed (110) facets to enhance pore-mouth shape-selectivity and reduce internal diffusion resistance.

Research on heteroatom-modified ZSM-22 remains limited, with challenges in achieving high loading and controlled positioning. Given the diversity of heteroatoms, it is essential to systematically investigate how synthesis parameters influence different doping pathways, and to establish a general model for the “parameter-dopant property” relationship to improve synthetic controllability.

In addition, while most laboratory studies use model reactants as probes, real fuel feedstocks are more complex and demand greater catalyst stability and tolerance. Thus, it is necessary to investigate how representative impurities (e.g., short-chain alkanes, naphthenes, and aromatics) affect the catalytic behavior of ZSM-22-based materials. Identifying the interaction sites of these

impurities and elucidating the competitive conversion mechanisms between real feed components and model compounds will be crucial for bridging fundamental studies with industrial applications.

CRedit authorship contribution statement

Qiang Wang: Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Ley Boon Sim:** Writing – original draft, Investigation, Conceptualization. **Ping Wang:** Visualization, Data curation. **Qiang Wang:** Writing – original draft, Investigation, Data curation, Conceptualization. **Bing-Hui Chen:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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