

The ZSM-22-ZSM-23 composite molecular sieve catalyst regulates the product distribution of the hydroisomerization of *n*-dodecane

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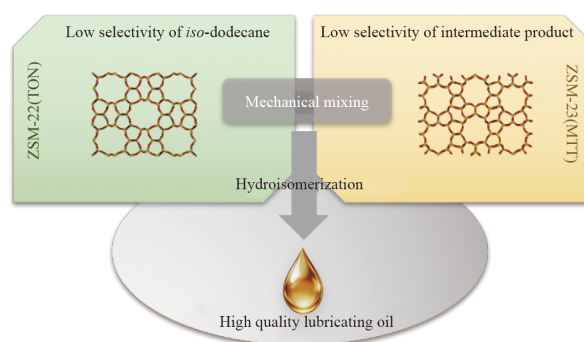
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Abstract: In this study, ZSM-22-ZSM-23 composite zeolite was synthesized *via* a mechanical mixing method. The morphology, acidic properties, and textural properties of the samples were characterized by XRD, SEM, TEM, NH₃-TPD, Py-FTIR, and N₂ adsorption-desorption techniques. The hydroisomerization catalytic performance of the composite zeolite was evaluated using *n*-dodecane as a model reactant, and compared against the individual zeolite components. It was found that the textural and acidic properties could be precisely modulated by varying the ZSM-22 to ZSM-23 mass ratio. At an optimal mass ratio of 4:1, the selectivity for *iso*-dodecane increased by 24% relative to ZSM-23, while the ratio of terminal-branching to intermediate-branching product selectivity (s_t/s_i) decreased by 14% compared to ZSM-22. The results demonstrate that the composite zeolite combines the advantages of both individual zeolite in terms of texture and acidity, exhibits superior hydroisomerization performance, and can effectively regulate the distribution of terminal-branching and intermediate-branching isomers in *iso*-dodecane.

Key words: ZSM-22; ZSM-23; composite molecular sieves; hydrogenation isomerization; *n*-dodecane



With the increasingly intense competition in the lubricant market, improving product quality is paramount for sustaining a competitive edge^[1–2]. The hydroisomerization of *n*-alkanes to branched alkanes, characterized by high lubricant base oil yield^[3], low viscosity and evaporation loss, superior oxidation stability, and good low-temperature fluidity^[4–5], is an effective strategy for enhancing lubricant quality^[6–7]. Consequently, optimizing the hydroisomerization performance of *n*-alkanes is critical for the production of high-quality lubricants^[8–9]. Ideally, this

process is driven by bifunctional catalysts, which combine metallic and acidic functions^[10]. The metal sites, typically provided by noble metals (e.g., Pt, Pd) or non-noble metals (e.g., Co, Ni), facilitate hydrogenation/dehydrogenation, while the acid sites—derived principally from zeolites, amorphous silica-alumina, organic-inorganic hybrids, or metal oxides—catalyze skeletal isomerization^[11]. Among them, zeolite molecular sieves have been widely used as catalyst supports for *n*-alkane hydroisomerization, such as SAPO molecular sieves^[12–14], aluminosilicate zeolites^[15–17],

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and mesoporous molecular sieves^[18–20]. *n*-Alkanes and *iso*-alkenes undergo dehydrogenation and hydrogenation reactions on the metal sites, respectively, while *n*-alkenes undergo protonation and skeletal isomerization on the acid sites. The isomerization process typically proceeds *via* two reaction mechanisms: the “pore-mouth” type and the “key-lock” type^[21–22]. The “pore-mouth” mechanism restricts the reaction to the channel entrance, favoring terminal methyl-branched isomers^[23]. In contrast, the “key-lock” mechanism allows the alkane chain to align within the pore channel, selectively yielding centrally branched isomers^[24].

In recent years, composite zeolites have been extensively investigated due to their unique properties. Formed by combining two or more distinct zeolite phases *via* physical or chemical methods, these materials not only retain the intrinsic characteristics of their individual components but often exhibit synergistic effects that surpass the performance of single-phase zeolites. Currently, the synthesis methods for composite zeolites mainly include: seed-assisted method, mechanical mixing, one-step crystallization, two-step crystallization^[25] and director-assisted reassembly method^[26], among others. Among these methods, mechanical mixing is widely favored for its cost-effectiveness, operational simplicity, and the ability to precisely control component ratios while preserving the structural integrity of the individual zeolites. Several studies have validated the efficacy of this method. For instance, Zhang et al.^[27] mechanical mixing is widely favored for its cost-effectiveness, operational simplicity, and the ability to precisely control component ratios while preserving the structural integrity of the individual zeolites. Several studies have validated the efficacy of this method; Similarly, Liu et al.^[28] found that mixing Al-SBA-15 zeolite with USY zeolite reduced acid amount but significantly enhanced catalytic performance, achieving 99% selectivity for perhydroanthracene; Furthermore, Fan et al.^[29] demonstrated that a ZSM-5/SAPO-11 mixture possessed increased mesoporosity, which could accelerate mass diffusion, and exhibited a moderate acidity distribution with more pronounced synergy between Brønsted acid and Lewis acid sites.

ZSM-22 (TON topology, 0.45 nm × 0.55 nm) and ZSM-23 (MTT topology, 0.45 nm × 0.56 nm) possess similar one-dimensional 10-membered ring channels. Therefore, combining these two zeolites can integrate the advantages of both TON and MTT structures, potentially leading to superior hydroisomerization performance. Currently, methods for synthesizing ZSM-22-ZSM-23 composite zeolites mainly include hydrothermal synthesis^[30], microwave-assisted synthesis^[31], and low-template ultrasonic-assisted synthesis. However, these methods generally suffer from harsh conditions and difficulties in scale-up production. In this work, a ZSM-22-ZSM-23 composite was prepared *via* a facile mechanical mixing route. Its synergistic effects in the hydroisomerization of *n*-dodecane and its influence on the isomer distribution were investigated, and its catalytic performance was compared with that of the individual zeolites.

1 Experimental

1.1 Chemicals

Deionized water (lab-made), fumed silica (SiO₂, 100%, Wacker), aluminum sulfate octadecahydrate (Al₂(SO₄)₃·18H₂O, AR, Tianjin Kermel), sodium aluminate (NaAlO₂, AR, Macklin), sodium hydroxide (NaOH, AR, Tianjin Kermel), potassium hydroxide (KOH, AR, Tianjin Kermel), pyrrolidine (PY, (CH₂)₄NH₂, AR, Aladdin), isopropylamine (IPA, C₃H₉N, CP, Aladdin), 1,6-hexanediamine (HDA, C₆H₁₅N₂, AR, Aladdin), chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, AR, Aladdin), *n*-dodecane (C₁₂H₂₆, GC, Aladdin).

1.2 Catalyst preparation

ZSM-22 zeolite was synthesized *via* a hydrothermal method. According to the molar ratio of $n(\text{Al}_2\text{O}_3):n(\text{SiO}_2):n(\text{KOH}):n(\text{HDA}):n(\text{H}_2\text{O}) = 1:80:15:27:3600$, designated amounts of KOH, Al₂(SO₄)₃·18H₂O, and HDA were successively added to deionized water and stirred for 30 min to form a homogeneous solution. Then, a designated amount of fumed silica was added, and stirring was continued for 3 h to achieve complete dissolution, yielding an initial gel. This gel was transferred into a stainless-steel autoclave lined with polytetrafluoroethylene (PTFE) and crystallized under static conditions at 160 °C for 48 h. The crystallized product was separated by centrifugation, filtered, washed with deionized water until neutral pH, and dried overnight at 90 °C. Subsequently, the obtained powder was calcined at 550 °C for 8 h to remove the organic structure-directing agent, yielding the Na-form ZSM-22. Finally, the Na-ZSM-22 was subjected to three consecutive ion exchanges with a 1 mol/L NH₄Cl solution (each for 2 h) at 80 °C, followed by calcination at 550 °C for 6 h to obtain H-ZSM-22.

ZSM-23 zeolite was synthesized *via* hydrothermal synthesis. With the molar ratio $n(\text{Al}_2\text{O}_3):n(\text{SiO}_2):n(\text{NaOH}):n(\text{PY}):n(\text{IPA}):n(\text{H}_2\text{O}) = 1:80:6.9:29:75:3800$, designated amounts of NaOH and fumed silica were successively added to deionized water to form Solution A. Separately, designated amounts of NaAlO₂, PY, and IPA were added to deionized water to form Solution B. After each solution was stirred vigorously for 40 min, Solution B was slowly added into Solution A. The mixture was stirred for another 3 h to obtain the initial gel. The gel was loaded into a PTFE-lined stainless-steel autoclave and crystallized under dynamic conditions at 180 °C with a rotation speed of 40 r/min for 48 h. The crystallized product was recovered by centrifugation, filtered, washed to neutrality and dried overnight at 90 °C. The dried powder was calcined at 550 °C for 8 h to burn off the organic templates, producing the Na-form ZSM-23. Finally, the Na-ZSM-23 was ion-exchanged three times with a 1 mol/L NH₄Cl solution (each for 2 h) at 80 °C, followed by calcination at 550 °C for 6 h to obtain H-ZSM-23.

H-ZSM-22 and H-ZSM-23 were ground together in an agate mortar for 30 min according to mass ratios of 1:4, 1:1 and 4:1, respectively, to obtain mechanically mixed composite zeolites. These were designated as HZ22-Z23-4-1-M, HZ22-Z23-1-1-M and HZ22-Z23-1-4-M, where “M” denotes mechanical mixing.

A predetermined volume of chloroplatinic acid solution (20 g/L) was added to γ - Al_2O_3 , followed by an appropriate amount of deionized water. The mixture was stirred at room temperature for 24 h. The sample was then dried overnight at 80 °C, followed by programmed calcination with a heating rate of 1 °C/min up to 400 °C, and held at this temperature for 4 h to finally obtain $\text{Pt}/\text{Al}_2\text{O}_3$. The five aforementioned H-form zeolites were each physically mixed with $\text{Pt}/\text{Al}_2\text{O}_3$ at a mass ratio of 1:1 by grinding. The resulting bifunctional catalysts were designated as $\text{Pt}/\text{HZSM-22}$, $\text{Pt}/\text{HZSM-23}$, $\text{Pt}/\text{HZ22-Z23-1-4-M}$, $\text{Pt}/\text{HZ22-Z23-1-1-M}$ and $\text{Pt}/\text{HZ22-Z23-4-1-M}$. The Pt loading was 0.5% for all catalysts.

1.3 Characterization

The hydroisomerization performance of the catalysts using *n*-dodecane was evaluated in a high-pressure fixed-bed microreactor system. First, 1.0 mL of catalyst (20–40 mesh) was loaded into a stainless-steel reactor tube. Before the reaction, the catalyst was activated under a hydrogen atmosphere at 400 °C for 4 h. Subsequently, under reaction conditions of temperature 260–360 °C, pressure 2.0 MPa, liquid hourly space velocity (LHSV) 3.3 h⁻¹ and H₂/hydrocarbon volume ratio of 363, the feed *n*-dodecane was introduced into the reaction system together with the carrier gas using an Elite EPP010 metering pump. After the reaction, gaseous products were directly analyzed by an online PANNA A91 gas chromatograph (GC). Liquid products were condensed, collected in a receiver, and subsequently analyzed by an offline PANNA A91 GC. The *n*-dodecane conversion, isomer selectivity, and isomer yield were defined by the following equations:

$$\text{Conversion (\%)} = \frac{n\text{-dodecane consumed}}{n\text{-dodecane in feedstock}} \times 100\% \quad (1)$$

$$\text{Isomer selectivity (\%)} = \frac{i\text{-dodecane formed}}{n\text{-dodecane consumed}} \times 100\% \quad (2)$$

$$i\text{-dodecane yield (\%)} = \frac{i\text{-dodecane formed}}{n\text{-dodecane in feedstock}} \times 100\% \quad (3)$$

2 Results and discussion

2.1 Characteristic results

The XRD patterns of the various samples are presented in

Figure 1. The XRD pattern of ZSM-22 exhibits characteristic diffraction peaks at $2\theta = 8.2^\circ$, 20.5° , 24.3° , 24.6° and 25.8° , corresponding to its TON structure. No extraneous peaks are detected, indicating the high phase purity of the as-synthesized ZSM-22 without any observable impurity phases. For ZSM-23, characteristic diffraction peaks ascribed to ZSM-23 zeolite are observed at $2\theta = 8.1^\circ$, 19.8° , 21.0° , 22.8° , 24.1° and 24.8° , which match well with the standard pattern of ZSM-23. The absence of additional reflections confirms the successful synthesis of pure-phase ZSM-23. The mechanically mixed samples, Z22-Z23-4-1-M, Z22-Z23-1-1-M and Z22-Z23-1-4-M, also exhibit characteristic diffraction peaks corresponding to both ZSM-22 and ZSM-23 zeolites at their respective positions, confirming the coexistence of the two zeolitic phases and demonstrating that mechanical blending does not alter their crystalline structures. Furthermore, as the mass fraction of ZSM-23 zeolite in the mixture, the intensity of the characteristic diffraction peaks attributed to ZSM-23 gradually increases, while the intensity of the peaks belonging to ZSM-22 correspondingly decreases.

Figure 2 presents the SEM images of the different samples. As shown in Figure 2(a), the ZSM-22 zeolite exhibits a rod-like morphology, with a length of approximately 2–3 μm and a width of about 0.3 μm . Figure 2 (e) shows that ZSM-23 zeolite appears as aggregates composed of stacked plate-like crystals, measuring roughly 1–2 μm in length and 0.8 μm in width. Observations from Figures 2(b)–(d) reveal that for the three mechanically mixed composite zeolites, ZSM-23 crystals adhere to the surfaces of ZSM-22 crystals. Furthermore, as the ZSM-23 content increases, the number of plate-like crystals adhering to the rod-like crystals progressively increases.

The TEM and elemental mapping images of the different samples are shown in Figure 3. The ICP characterization results listed in Table 1 indicate that the Pt loading for the catalysts is approximately 0.5%. It can be observed from Figure 3 that the elements Si, Al and Pt are uniformly distributed. Statistical analysis reveals that the average Pt particle sizes are comparable across the different catalysts, with measured diameters of 1.09 nm for $\text{Pt}/\text{ZSM-22}$, 1.02 nm for $\text{Pt}/\text{Z22-Z23-1-1-M}$ and 1.03 nm for $\text{Pt}/\text{ZSM-23}$.

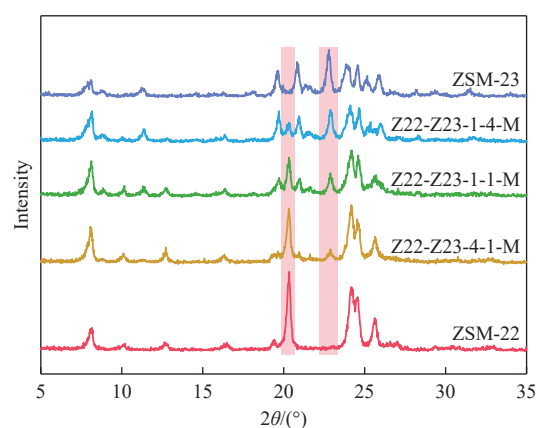
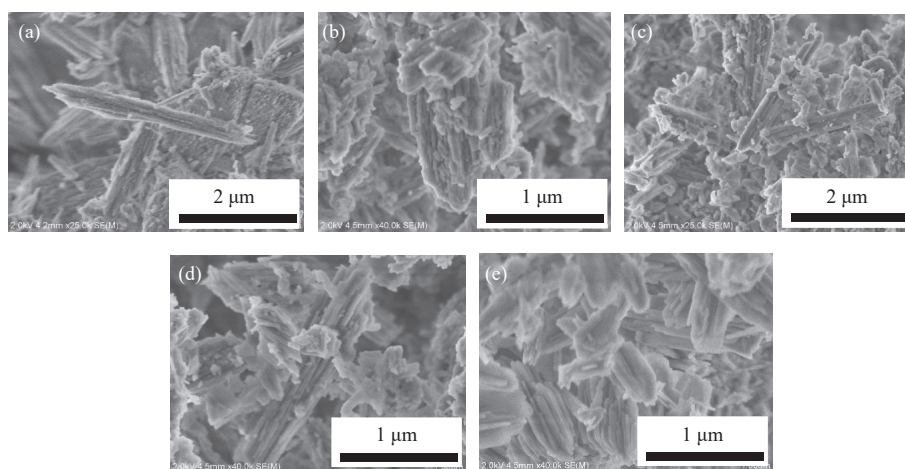
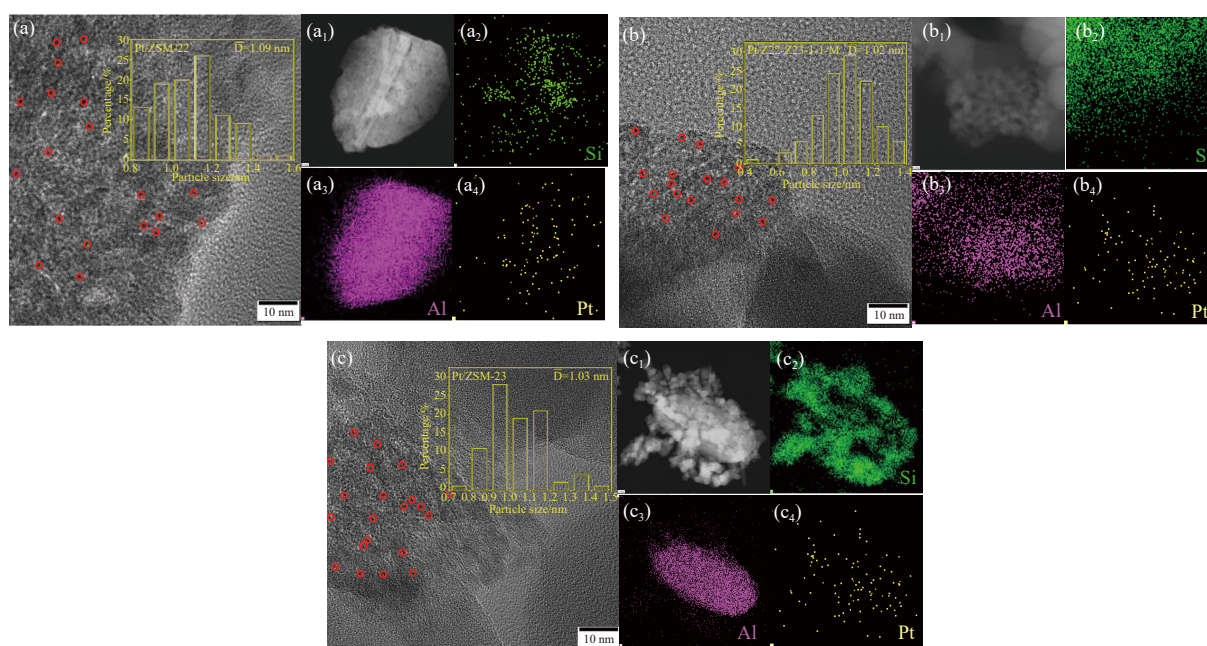


Fig. 1 XRD patterns of different samples



(a): ZSM-22; (b): Z22-Z23-4-1-M; (c): Z22-Z23-1-1-M; (d): Z22-Z23-1-4-M; (e): ZSM-23.

Fig. 2 SEM images of different samples



(a): Pt/HZSM-22; (a₁)–(a₄) Pt/HZSM-22 mapping images; (b): Pt/HZ22-Z23-1-1-M; (b₁)–(b₄) Pt/HZ22-Z23-1-1-M mapping images; (c): Pt/HZSM-23; (c₁)–(c₄) Pt/HZSM-23 mapping images.

Fig. 3 TEM and mapping images of different samples

Table 1 ICP results of different samples

Sample	Pt/%
Pt/HZSM-22	0.50
Pt/HZ22-Z23-1-1-M	0.51
Pt/HZSM-23	0.50

Figure 4 displays the NH_3 -TPD (a) and Py-FTIR (b) spectra of different samples, and the calculated acid amounts of the five zeolites are listed in Table 2. In NH_3 -TPD profiles, the desorption temperature reflects acid strength, while the peak area corresponds to the concentration of acid sites^[32]. As shown in Figure 4(a), all samples display two distinct NH_3 desorption peaks centered

around 230 and 430 °C, assigned to weak and strong acid sites, respectively. The total acid site density increases in the order: HZSM-22 < HZ22-Z23-4-1-M < HZ22-Z23-1-1-M < HZ22-Z23-1-4-M < HZSM-23. Relative to HZSM-23, the composite zeolites HZ22-Z23-1-4-M, HZ22-Z23-1-1-M and HZ22-Z23-4-1-M show reductions in total acid amount of 6.49%, 7.55% and 10.22%, respectively. Considering the difference in crystal size between HZSM-22 and ZSM-23, it is speculated that the dispersion and coverage of ZSM-23 on the ZSM-22 surface after mechanical mixing lead to the reduction in strong acid amount, which is consistent with the SEM observations. As shown in Figure 3(b), all samples exhibit three infrared absorption bands in the 1400–1600 cm^{-1} region at desorption temperatures of 150, 250 and 350 °C.

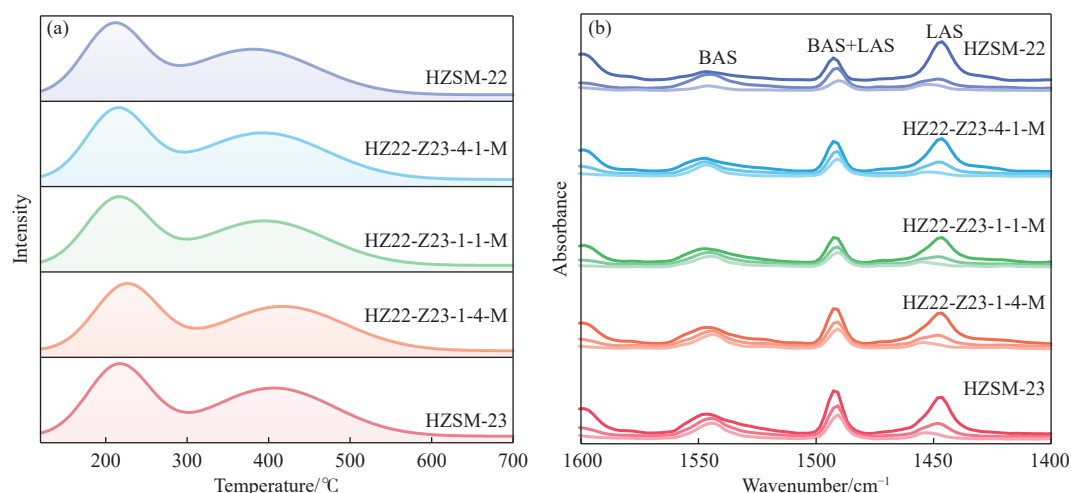


Fig. 4 NH_3 -TPD of different samples (a) and Py-FTIR spectra at different desorption temperatures of 150 °C (dark line), 250 °C (middle dark line), 350 °C (light line) (b)

Table 2 Acid amount of different samples

Sample	Total acid ^a /($\mu\text{mol} \cdot \text{g}^{-1}$)	Brønsted acid ^b /($\mu\text{mol} \cdot \text{g}^{-1}$)			Lewis acid ^b /($\mu\text{mol} \cdot \text{g}^{-1}$)		
		150 °C	250 °C	350 °C	150 °C	250 °C	350 °C
HZSM-22	470.1	16.4	10.2	5.9	38.5	16.3	6.0
HMZ22-23-4-1	490.0	26.6	19.2	14.0	36.0	12.2	4.6
HMZ22-23-1-1	504.6	33.4	26.2	19.5	34.3	11.6	6.3
HMZ22-23-1-4	510.4	34.6	25.8	20.5	38.0	13.3	6.9
HZSM-23	545.8	38.8	29.1	22.4	34.3	13.1	5.9

^a: Obtained by NH_3 -TPD; ^b: Obtained by Py-IR.

The absorption band at 1540 cm^{-1} is attributed to pyridine adsorbed on Brønsted (B) acid sites, the band at 1450 cm^{-1} to pyridine adsorbed on Lewis (L) acid sites, and the band at 1490 cm^{-1} is associated with pyridine interacting with both B and L acid sites. The characterization results indicate that the Brønsted acid amount of the mechanically mixed samples lies between those of the two individual zeolites, HZSM-22 and HZSM-23, suggesting that the acidity results from the combined contribution of both components. This conclusion is corroborated by the NH_3 -TPD data.

The N_2 adsorption-desorption isotherms and the corresponding BJH pore size distribution curves for various samples are shown in Figures 5(a) and (b), respectively, while their detailed textural parameters are listed in Table 3.

As shown in Figure 5(a), all five zeolites exhibit typical Type I isotherms, characterized by a sharp uptake at low relative pressures ($p/p_0 < 0.01$), indicating the presence of micropores. The pore-size distributions derived from the adsorption branches (Figure 5(b)) are mainly concentrated in the range of 0.5–1.5 nm, further confirming the microporous nature of the materials. As can be seen from Table 3, the five zeolites possess identical micropore volumes. The external surface area, total pore volume, and mesopore volume of the three mechanically mixed composite zeolites with different ratios all fall between those of the individual HZSM-22 and HZSM-23 zeolites, and increase with a higher proportion of ZSM-23.

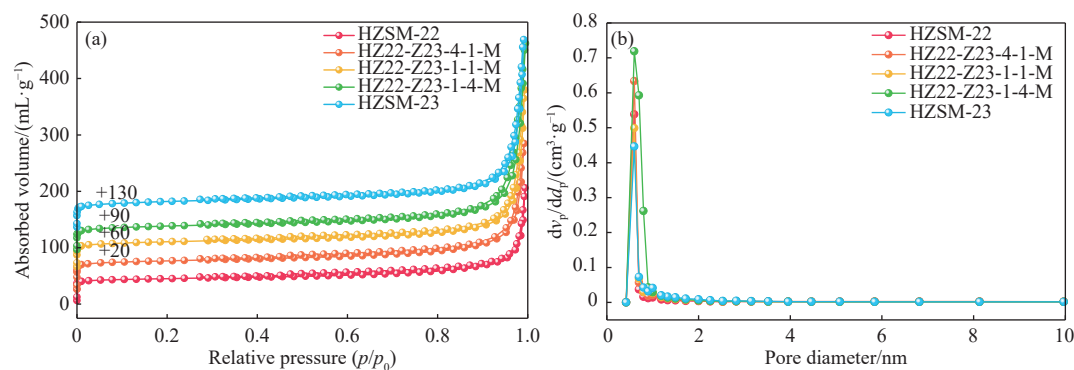


Fig. 5 N_2 adsorption-desorption isotherms (a) and BJH pore size distribution (b)

Table 3 Pore structure parameters of different samples and Si/Al

Sample	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$S_{\text{Mic}}^a/(\text{m}^2 \cdot \text{g}^{-1})$	$S_{\text{Ext}}/(\text{m}^2 \cdot \text{g}^{-1})$	$v_{\text{Total}}^b/(\text{cm}^3 \cdot \text{g}^{-1})$	$v_{\text{Mic}}^a/(\text{cm}^3 \cdot \text{g}^{-1})$	$v_{\text{Meso}}/(\text{cm}^3 \cdot \text{g}^{-1})$	Si/Al
HZSM-22	176	145	31	0.24	0.06	0.18	41
HZ22-Z23-4-1-M	216	177	39	0.35	0.06	0.29	—
HZ22-Z23-1-1-M	192	150	42	0.42	0.06	0.36	40
HZ22-Z23-1-4-M	183	139	44	0.48	0.06	0.42	—
HZSM-23	193	148	45	0.50	0.06	0.44	41

^a: t -plot method; $S_{\text{Mic}} = S_{\text{BET}} - S_{\text{Ext}}$; $v_{\text{Mic}} = v_{\text{Total}} - v_{\text{Meso}}$; ^b: Volume adsorbed at $p/p_0 = 0.99$.

Due to the relatively large crystal size of HZSM-22, its specific surface area is lower. The BET specific surface areas of the other four zeolites are all approximately 200 m²/g. Therefore, by mechanically mixing ZSM-22 and ZSM-23 zeolites, the external surface area, total pore volume, and mesopore volume of the composite zeolites can be tuned. Moreover, the measured Si/Al ratios are approximately 40, in good agreement with the nominal composition of the initial synthesis gel.

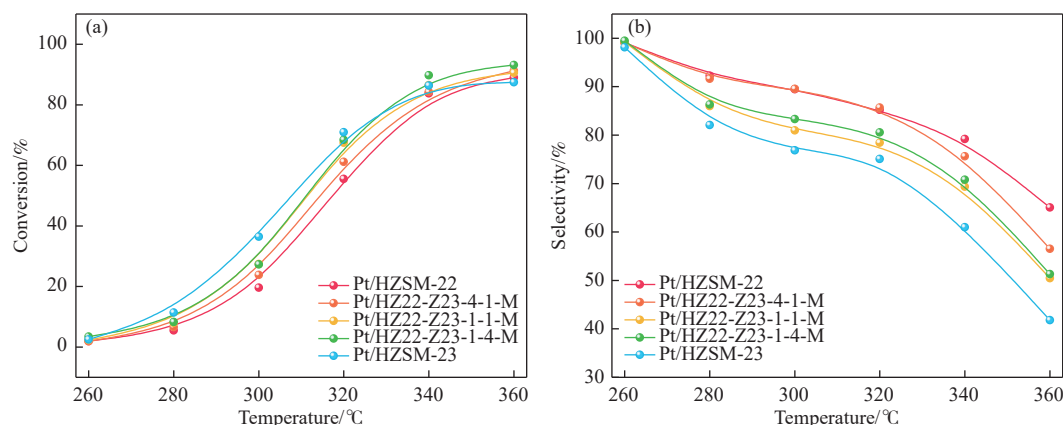
2.2 Characteristic results

The catalytic performance of the five different catalysts for *n*-dodecane hydroisomerization is presented in Figure 6. As seen from Figure 6(a), in the temperature range of 280–320 °C, the *n*-dodecane conversion decreases in the order: Pt/HZSM-23 > Pt/HZ22-Z23-1-4-M > Pt/HZ22-Z23-1-1-M > Pt/HZ22-Z23-4-1-M > Pt/HZSM-22. This order coincides with the descending sequence of Brønsted acid site density on the corresponding zeolite supports, confirming that the population of Brønsted acid sites, which serve as active centers for hydroisomerization, plays a determining role in the catalytic activity. Figure 6(b) illustrates the *iso*-dodecanes selectivity as a function of temperature. For all five catalysts, isomer selectivity decreases with increasing temperature. The selectivity values of the three mechanically mixed catalysts generally lie between those of the two individual catalysts. The Pt/HZSM-23 catalyst exhibits the lowest *iso*-dodecane selectivity, which is attributed to the higher proportion of

strong acid sites, thereby promoting cracking reactions. These results suggest that the introduction of an appropriate amount of ZSM-22 into ZSM-23 can effectively enhance the *iso*-dodecane selectivity.

Figure 7 shows the relationship between *iso*-dodecane yield and temperature for the five catalysts. Below 320 °C, the Pt/HZSM-23 catalyst exhibits the highest *iso*-dodecane yield. As the reaction temperature increases, cracking reactions become more pronounced, leading to a decline in its *iso*-dodecane yield at an earlier stage. In contrast, the Pt/HZSM-22 catalyst achieves its maximum yield of 66.37% at 340 °C. The three mechanically mixed catalysts with different ratios combine the acidity advantages of Pt/HZSM-22 and Pt/HZSM-23 as well as their textural advantages. Consequently, their isomer yields lie between those of the Pt/HZSM-22 and Pt/HZSM-23 catalysts.

Figure 8 shows the distribution of mono-branched isomer products of *n*-dodecane at 320 °C as a function of the ZSM-22/ZSM-23 mechanical mixing ratio. The product distribution reveals that over Pt/HZSM-22, the mono-branched isomers are predominantly 2-methylundecane (terminal branching), while Pt/HZSM-23 favors the formation of 5-methylundecane (central branching). Consequently, with increasing ZSM-23 content in the composite, the selectivity to 2-methylundecane first increases and then decreases, whereas that to 5-methylundecane shows a monotonic increase with a gradually diminishing rate. The selectivities to 3-methylundecane and 4-methylundecane stabilize after the ZSM-22:ZSM-23 mass ratio exceeds 1:1.


 Fig. 6 The conversion of *n*-dodecane (a) and the selectivity of *iso*-dodecane of different catalysts (b)

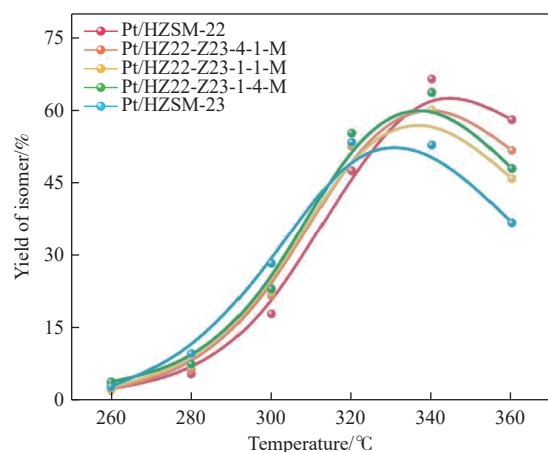


Fig. 7 The yield of *iso*-dodecane of different catalysts

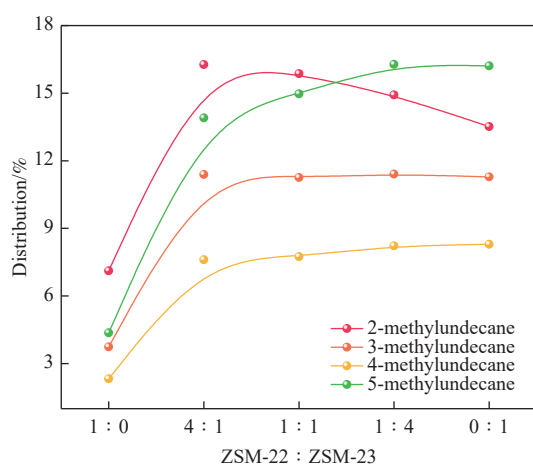


Fig. 8 At 320 °C the isomerization of *n*-dodecane products of mono-branched chain of different catalysts changed

The selectivity towards mono-branched and double-branched chain isomerization products obtained over the five catalysts is compared in Figure 9. It can be observed from the figure that the three mechanically mixed catalysts

with different ratios exhibit lower selectivity to mono-branched isomers compared to the two individual catalysts, but they show higher selectivity to double-branched isomers. Typically, isomer products with a higher degree of branching impart lower pour points and cloud points to lubricant base oils, thereby enhancing their low-temperature flow properties. Thus, the catalysts prepared by mechanical mixing can effectively upgrade the quality of lubricant base oils.

Figure 10 presents the selectivity ratio of terminal-branching to internal-branching for both mono-branched and double-branched isomers (s_t/s_i) produced over the five catalysts. As seen in Figure 10(a), the s_t/s_i ratio for mono-branched isomers decreases with increasing reaction temperature for all five catalysts. The Pt/HZSM-22 catalyst shows a higher propensity to produce terminal-branched isomers. Within the 280–320 °C range, the mono-branched s_t/s_i ratios for the three mechanically mixed catalysts lie between those of the Pt/HZSM-22 and Pt/HZSM-23 catalysts. Figure 10(b) indicates that above 320 °C, a similar intermediate trend is observed for the double-branched s_t/s_i ratios of the mixed catalysts. These results indicate that ZSM-22 operates *via* a “pore-mouth” isomerization mechanism, favoring terminal branching, while ZSM-23 operates *via* a “key-lock” mechanism that promotes internal branching.

At a reaction temperature of 320 °C, a stability evaluation was conducted for the Pt/HZ22-Z23-4-1-M catalyst, which exhibited the highest *iso*-dodecane yield. The experimental results are shown in Figure 11. The catalyst maintained a stable *n*-dodecane conversion of about 78% throughout the time-on-stream test. Correspondingly, the *iso*-dodecane selectivity and yield remained nearly constant at approximately 80 % and 59 %, respectively. The experimental results demonstrate that the Pt/HZ22-Z23-4-1-M catalyst possesses excellent stability under prolonged reaction conditions.

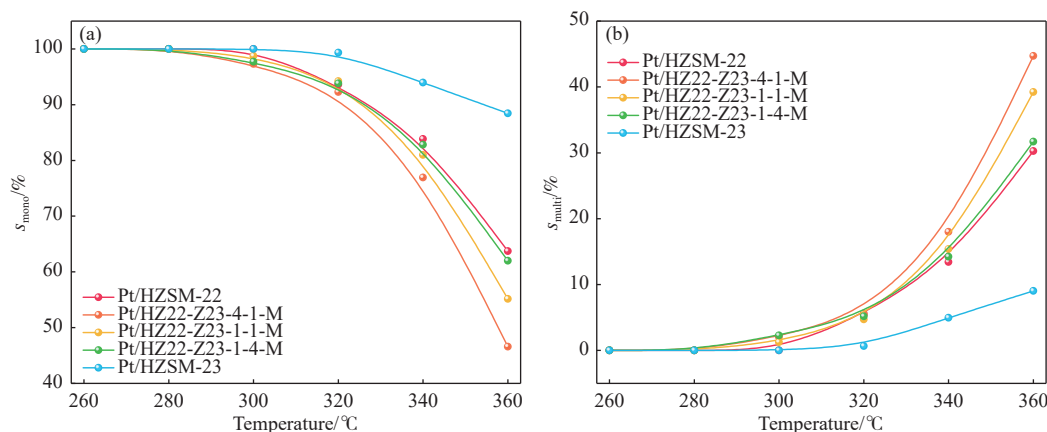


Fig. 9 The selectivity of mono branched chain isomerization products (a) and the selectivity of double-branched chain isomerization products of different catalysts (b)

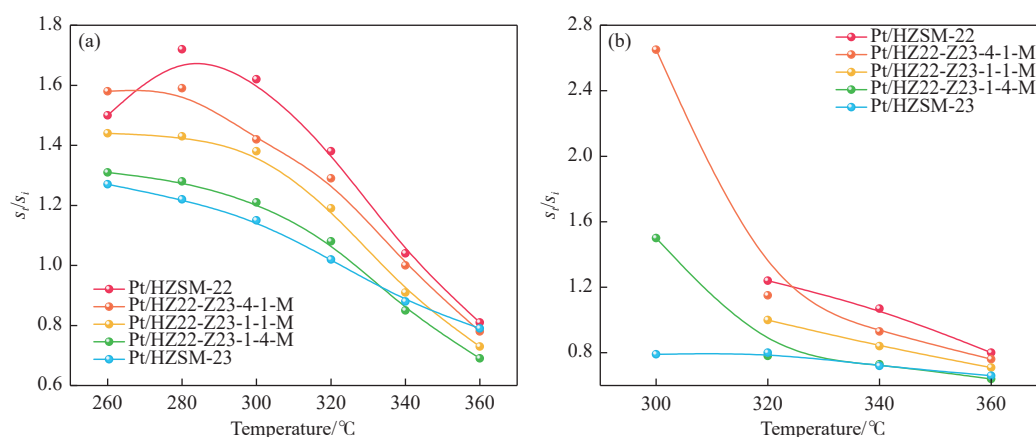


Fig. 10 The variation of s_i/s_j in mono-branched isomers (a) and double-branched isomers (b)

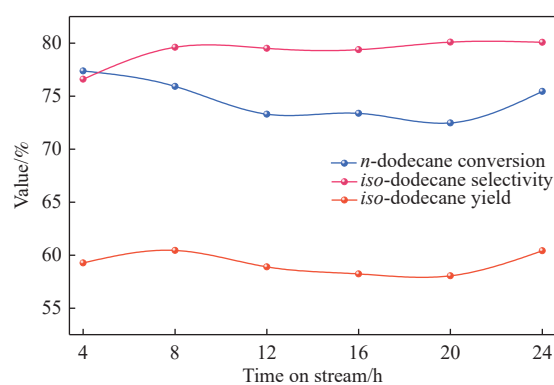


Fig. 11 Temporal evolution of the catalytic performance of Pt/HZ22-Z23-4-1-M

Table 4 compares the performance of recently reported bifunctional catalysts with mechanically mixed composite zeolite supports for n -alkane hydroisomerization. The supports of all four catalysts were prepared by mechanical mixing, and n -dodecane was used as the model reactant. As can be seen from the table, the Pt/ZSM-22-ZSM-23-M catalyst prepared in this work exhibits the highest iso -dodecane yield. This superior performance highlights that the mechanical blending of ZSM-22 and ZSM-23, which combines their distinct topological features, represents an effective strategy for enhancing the hydroisomerization performance of bifunctional catalysts.

Table 4 Comparison of catalytic performance for recent composite zeolites

Catalyst	Support preparing method	Reaction conditions	Model compound	Maximum isomer yield/%	Core characteristics	Reference
Pt/ZSM-22-ZSM-23-M	Mechanical mixing	2.0 MPa LHSV = 3.3 h ⁻¹ hydrogen/hydrocarbon volume ratio = 363	n -dodecane	64	Higher isomer selectivity and higher degree of isomer branching	this work
Pt/MOR+SAPO-11	Mechanical mixing	2.0 MPa LHSV = 2.0 h ⁻¹ hydrogen/hydrocarbon volume ratio = 200	n -dodecane	49	Higher isomer yield	[33]
Pt/ZSM-22/ZSM-48-M	Mechanical mixing	2.0 MPa LHSV = 2.0 h ⁻¹ hydrogen/hydrocarbon volume ratio = 600.	n -dodecane	63	Higher isomer selectivity	[34]
Pt/SAPO-11+Beta	Mechanical mixing	2.0 MPa LHSV = 2.0 h ⁻¹ H ₂ / n -dodecane molar ratio=2	n -dodecane	50	Maximum yield for multi-branched isomers	[35]

3 Conclusion

In this work, ZSM-22-ZSM-23 composite zeolites with different ratios were prepared *via* mechanical mixing. Characterization analyses indicated that the total number of

acid sites and the pore volume of the composites increased progressively with the rising content of ZSM-23. Catalytic evaluation in n -dodecane hydroisomerization demonstrated that Pt/HZSM-22 preferentially produced terminally branched isomers, while Pt/HZSM-23 mainly generated isomers with internal branching. By adjusting the composite

ratio, an isomer product distribution intermediate between those of the two individual zeolites was successfully achieved. This effectively balances the respective limitations of Pt/HZSM-23 (relatively low isomer selectivity) and Pt/HZSM-22 (limited ability to produce internal-branched products). This indicates that mechanical mixing can integrate the topological characteristics of ZSM-22 and ZSM-23, enabling flexible control over the distribution of terminal- and internal-branched isomers in *iso*-dodecane. Consequently, it provides an effective strategy for obtaining high-performance lubricant base oils.

Declaration of Competing Interest

The authors declare no conflict of interest.

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ZSM-22-ZSM-23 复合分子筛催化剂调节正十二烷临氢异构化产物分布

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摘 要: 本研究通过机械混合的方法, 制备出了 ZSM-22-ZSM-23 复合分子筛。采用 XRD、SEM、TEM、NH₃-TPD、Py-FTIR 及 N₂ 吸附-脱附等方法对样品的形貌、酸性质、织构性质等进行表征, 并以正十二烷为模型反应物, 对比研究了其与两种单一分子筛的临氢异构催化性能。通过改变 ZSM-22 和 ZSM-23 分子筛的质量比, 可以有效调节分子筛的部分织构性质和酸性质; 当 ZSM-22 与 ZSM-23 质量比为 4:1 时, 异构十二烷的选择性较 ZSM-23 提高了 24%, 端位支链与中间位支链产物选择性之比 (*s*/*s*) 较 ZSM-22 降低了 14%。结果表明, 该复合分子筛结合了两种单一分子筛在织构与酸性质方面的优势, 表现出更优异的临氢异构化性能, 可有效调节异构十二烷中端位与中间位异构体的分布。

关键词: ZSM-22; ZSM-23; 复合分子筛; 临氢异构化; 正十二烷

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