Synthesis of ZSM-23 Zeolite by Two-Stage Temperature-Varied Crystallization and Its Isomerization Performance

Xiaoyan Chen 1, Hongjuan Xi 1,2,*, Congbiao Chen 1, Zhongyi Ma 1 and Bo Hou 1,*

1 State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China; chenxiaoyan@sxicc.ac.cn (X.C.); congbiao_chen@sxicc.ac.cn (C.C.); mazhgyi@sxicc.ac.cn (Z.M.)
2 Dalian National Laboratory for Clean Energy, Dalian 116023, China
* Correspondence: xhj20050314@sxicc.ac.cn (H.X.); houbo@sxicc.ac.cn (B.H.);
Tel.: +86-0351-4040428 (H.X. & B.H.)

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Abstract: Several ZSM-23 zeolites with different acid distributions are synthesized by two-stage temperature-varied crystallization and changing the species of aluminum source via conventional hydrothermal synthesis. The crystallinity, micropores, external specific surface area and the Si/Al ratios are measured by XRD, BET, ICP and XPS, indicating that both the body phase and the surface of the zeolite synthesized by two-stage temperature-varied crystallization have higher Si/Al ratio, and the zeolite synthesized with aluminum nitrate as the aluminum source exhibit the largest specific surface area. The properties of acidity and Pt obtained by NH3-TPD, TEM, Py-IR and H2-TPR show that the suitable B-acid distribution leads to high Pt dispersion over the zeolite. Applying these catalysts to the isomerization of n-dodecane, the zeolite synthesized with aluminum sulfate as aluminum source by two-step temperature-varied crystallization shows the best isomerization performance, that the selectivity of i-dodecane reaches 81.2% at 90.7% conversion. Therefore, the matching of acidity, external specific surface area and Pt dispersion of the zeolites is the key to improve the isomerization performance of long-chain alkanes.

Keywords: ZSM-23 zeolite; two-stage temperature-varied; isomerization performance

1. Introduction

With the increasingly strict requirements of environmental protection laws and regulations and the rapid development of the automobile industry, the demand for new mechanical equipment for high-quality lubricating oil is increasing gradually, leading to higher quality requirements for oil products [1]. As a result, the development of low sulfur, low ash, high oxidation resistance, low volatility and good viscosity is imperative. Therefore, isomerization dewaxing technology is known as an important technological progress in the field of petroleum refining in recent years [2], and the core technology is the hydroisomerization catalyst.

The hydroisomerization of long-chain n-alkanes is mainly carried out on bifunctional catalysts. The isomerization performance of bifunctional catalysts is determined by the properties of acid carrier, metal properties and the synergistic of metal and acid carrier. The acid sites of zeolites provide isomerization function and metal sites provide hydrogenation/dehydrogenase functions [3,4]. As a metal center, Pt has good hydrogenation/dehydrogenation performance, which can rapidly saturate olefins and avoid coking and capping acid centers. Guo [5] et al. Studied the performance of Pt supported SAPO series and ZSM-5, ZSM-22 and ZSM-23 catalysts in n-octane hydroisomerization. The results showed that ZSM-23, one-dimensional mesoporous zeolite, had high selectivity for isomers.
and could effectively reduce cracking. However, many studies [6–8] have confirmed that if the content of Pt is high enough, the rearrangement of C-C bonds at acid sites is the rate-determining step of this reaction scheme. Hence, the performance of zeolite catalysts is closely related to the acid sites; however, the acidic characteristics of zeolites originate from the sitting position and distribution of framework Al, which depends on the conditions of zeolite synthesis [9].

Angell et al. [10] studied the aging stage of a type (LTA) zeolite at the early stage of crystallization, and found that when the primary gel was heated to 96 °C, Al(OH)₄⁻ in the liquid phase almost entirely condensed with silicic acid ions to form a secondary gel for relatively tight structure. At this time, the solid content increased and the average particle size became smaller. The importance of solution (gel) chemistry for the specific zeolites properties has long been recognized [11,12]. However, Rumar et al. [13,14] found that the addition of oxygen-containing anions can significantly enhance the nucleation and crystallization during the synthesis of the zeolites. These anions play a catalytic role in nucleation during crystallization. Petrik [15] reported the NO₃⁻ anion provided a consistently more alkaline environment than the SO₄²⁻, which affected the morphology, pore size distribution and catalytic activity of ZSM-5. Thus, it is speculated that different aluminum sources can be used to introduce different anions into the reaction gel system, which will affect the physical and chemical properties of zeolites, such as size, morphology and acid properties.

In past studies, heteroatoms were introduced into zeolite framework [16] and promoter [17] were added into the catalyst to improve the isomerization performance of ZSM-23. Liang et al. [18] synthesized a series of Fe-substituted ZSM-23 samples with higher n-hexadecane isomerization selectivity. B [19] and Mg [17] have also been introduced into ZSM-23 zeolite to reduce the content of B acids and exhibited high isomerization performance. In general, the heteroatoms introduced were easy to come off the zeolite framework showed low catalytic activity in these reactions. While, ZSM-23 was synthesized by dual structure directing agents for n-hexadecane isomerization [20], and its reactive activity was also lower than that of the zeolite synthesized with pyrrolidine as structure directing agents. However, in the presence of strong acid sites, catalysts with high activity and enhanced selectivity are much less investigated. Therefore, it is necessary to adjust the acid distribution of zeolite from the synthesis of zeolite to improve the isomerization performance of ZSM-23.

Obviously, the distribution of acid center positions was formed by Al replacing Si at different lattice sites, which leads to the different reaction environment and shape selectivity around the active site. In our research, the ZSM-23 zeolites with different acid sites distributions were synthesized by changing the preparation parameters. Additionally, the effects of anion species and different crystallization methods on pore volume distribution, acidity, morphology and catalytic activity of zeolites were investigated. Furthermore, the influence of acid distribution of ZSM-23 and Pt dispersion on the isomerization performance were studied by using n-dodecane isomerization as a probe reaction.

2. Materials and Methods

2.1. Synthesis of ZSM-23 Zeolites with Different Properties

In the experiment, three different synthetic schemes were introduced to regulate the acid distribution of ZSM-23 zeolite. We used pyrimidine (Aldrich, 99%) as structure directing agents (SDA), LUDOX HS-40 (Aldrich, 40%) as aluminum source, aluminum nitrate (Sinopharm Chemical Reagent Co., Shanghai, China) and aluminum sulfate (Sinopharm Chemical Reagent Co., 99%) as aluminum source, and sodium hydroxide (Sinopharm Chemical Reagent Co., 96%) as alkali source. A homogeneous reaction mixture with a molar ratio of 1.0 SiO₂: 0.06 Na₂O: 0.036 Al₂O₃: 0.11 SDA: 45 H₂O was finally obtained.

Scheme I. First, the ZSM-23 zeolite was synthesized by adding deionized water, amorphous silica, pyrimidine and aluminum sulfate slowly in sequence under stirring at room temperature, then transferred the above gel into a Teflon-lined steel autoclave and aged it at 100 °C for 10 h, and crystallized by hydrothermal treatment at 180 °C for 36 h under rotating, collected the products, denoted as ZS-1.
Scheme II. The preparation of synthetic gel was the same as scheme I except that no pre-aging was carried out, denoted as ZS-2.

Scheme III. The composition and preparation of synthetic gel were similar as the scheme II, only the aluminum nitrate was used instead of aluminum sulfate, and the hydrothermal crystallization time was 54 h at 180 °C, denoted as ZN-1.

2.2. Preparation of Catalysts

The solid zeolites obtained above were washed with deionized water, filtered, dried at 120 °C overnight, then calcined at 550 °C for 20 h. Next, the ZSM-23 products were treated with 1 M NH₄NO₃ solution by ion exchange for three times at 80 °C for 12 h, then calcined at 550 °C for 8 h to obtain the proton form, denoted as H-ZS-1, H-ZS-2, H-ZN-1, respectively. The samples in protonic form were impregnated in an aqueous solution of H₂PtCl₆·6H₂O (Aldrich, Pt ≥ 37.5%) overnight, dried at 110 °C for 4 h and calcined at 420 °C for 4 h. Bifunctional catalysts with 0.5 wt. % Pt were obtained, denoted as Pt/H-ZS-1, Pt/H-ZS-2, Pt/H-ZN-1, respectively. Additionally, the catalysts after the reaction were denoted as Re-Pt/H-ZS-1, Re-Pt/H-ZS-2, Re-Pt/H-ZN-1, respectively.

2.3. Characterization

The phase purity and crystallinity of the samples were characterized using powder X-ray diffraction by a PANalytical X’Pert³ diffractometer loaded with Cu-Kα radiation (40 kV, 40 mA, λ = 1.5418 Å). The morphology of the samples was characterized with a JSM-7001F field emission scanning electron microscope (SEM). Aggregation state and particle size of Pt were measured transmission electron microscope (TEM) images using a Tecnai G2 F20 S-Twin instrument. Elemental composition of the samples was obtained using ICP-OES apparatus (Thermo Scientific iCAP 7000 Series), after dissolving the ZSM-23 zeolites in strong acidic solution. XPS is widely used for the determination of the surface chemical composition, which was carried out on a Thermo ESCALAB 250XI spectrometer, using an aluminum K Alpha (hv = 1486.6 eV) as the X-ray source, operating at 150 W. The external surface area, microporous volume, and microporous area were determined by the t-plot method. Basic properties of the different samples were carried out by N₂ physisorption measurements on a Micromeritics ASAP 2460 at −196 °C. The coordination structure of the Al was detected by NMR to determine whether the Al entered the zeolite framework. ²⁷Al MAS NMR were recorded by 4 mm probe, with a rotational speed of 13 kHz and resonance frequency of 156.4 MHz. Pt dispersion was measured by CO pulse adsorption on a TP-5080 chemical adsorption instrument. The average size of Pt particle was calculated by assuming that one CO molecule was adsorbed by a Pt atom. H₂-TPR was measured by the TP-5080, with TCD as detector for H₂. The acid strength of zeolites were measured by NH₃-TPD. The quantities of Brønsted and Lewis acid sites were estimated by pyridine adsorption Fourier-transform infrared (Py-FTIR) in the range of 1400–1600 cm⁻¹, and B acid on the outer surface of zeolites was measured by dTBPy on a Thermo NICOLET 6700.

2.4. Catalytic Performance Test

The n-dodecane isomerization was used as a model reaction in a fixed-bed reactor at a total pressure of 4 MPa, with liquid hourly space velocity (LHSV) of 1.2 h⁻¹ and a volumetric H₂/n-dodecane ratio of 750. Firstly, the bifunctional catalyst was reduced in situ for 4 h at 400 °C in a flow of H₂, then the reaction temperature was reduced to the initial reaction temperature, finally the n-dodecane was fed into the reactor under a certain flow rate. In the reaction test of each catalyst, 5 or 6 temperature points were taken for analysis. The products were collected every 24 h and the liquid products were analyzed using gas chromatography (Agilent HP-1).
3. Results and Discussion

3.1. Structure and Textural of ZSM-23 Zeolites

The XRD patterns of the different zeolites synthesized under different hydrothermal synthesis conditions are showed in Figure 1. All the samples present characteristic diffraction peaks of ZSM-23 [21], and no impurity phase is formed. The crystallinity of ZSM-23 zeolites synthesized with aluminum sulfate as silicon source is higher than that with aluminum nitrate as silicon source (Table 1). In addition, the ZS-1 has the highest crystallinity due to the low temperature pre-crystallization and SO$_4^{2-}$ anions, which introduces more silicon into the framework of zeolite.

![XRD patterns of different samples.](image)

**Table 1.** Textural properties of the different zeolites.

| Samples | Si/Al$^1$ | Si/A 1$^2$ | Si/Al$^3$ | Pt Particle Size nm$^4$ | Pt Dispersion$^5$ | Relative Crystallinity$^6$ % |
|---------|-----------|------------|-----------|------------------------|-------------------|-----------------------------|
| ZS-1    | 55        | 48.6       | 14.2      | 2.1                    | 50.9              | 100                         |
| ZS-2    | 55        | 46.2       | 13.8      | 2.5                    | 42.4              | 97.2                        |
| ZN-1    | 55        | 42.2       | 12.7      | 2.0                    | 53.5              | 93.5                        |

Si/Al represent the ratios of Si/Al. $^1$ Obtained by feed ratio of initial solutions. $^2$ Calculated using ICP-OES. $^3$ The value of Si/Al on the surface is obtained by XPS. $^4$ Obtained by chemical adsorption of CO. The average size of Pt particle was assumed to be uniform semispherical Pt particle. $^5$ Obtained by pulse adsorption of CO. $^6$ Obtained by using ZS-1 (100%) as a standard.

It is well known that the use of different raw materials and crystallization methods in zeolite synthesis will result in products with significantly different crystal sizes and shapes. The SEM and TEM images of three ZSM-23 zeolites are shown in Figure 2. The ZS-1 is formed by sheet cross polymerization with a length of 600–900 nm. This is due to the formation of a lot of crystal nucleus during aging and then aggregation. Sample ZS-2 presents the typical needle-shaped morphology of MTT zeolites [21] with a size of about 60 nm in diameter and above 1 μm in length. However, the sample ZN-1 shows the jujube core morphology, which is polymerized by lots of irregular flakes with length of about 40 nm.
The textural properties of the zeolites obtained are shown in Table 1. Different samples have the same feed ratio of Si/Al, while all samples have higher surface aluminum content than body phase. However, the Si/Al ratio of body phase and the surface of the zeolite prepared from using aluminum sulfate as aluminum source are higher than that prepared from using aluminum nitrate as aluminum source. This may be due to the fact that the presence of the SO$_4^{2-}$ inhibited the incorporation of Al\cite{15} into the ZSM-23 framework. And the value of Si/Al on the surface of zeolite was determined by XPS.

From the $^{27}$Al MAS NMR spectra (Figure 3), it can be seen that an intense signal appears at 54 ppm in all the samples, which is assigned to the four-coordinating Al, and no Al signal belonging to the extra-framework is detected at 0 ppm. It is indicated that the Al atoms of ZSM-23 obtained by the three schemes are almost in the framework of zeolite.
At P/P0 < 0.01, the adsorption amount of N2 molecules increase dramatically, and exhibit a type IV N2 isotherm, which show typical microporous structures (Figure 4). The increase of the curve at higher relative pressures is caused by the multi-layer adsorption of N2 on the surface of the zeolite. Compared with the other two samples, the hysteretic ring of H-ZN-1 is larger, which is due to the increase of mesoporous in zeolite composed of small flake crystals, consistent with the SEM and TEM images.

The basic properties of respective zeolite are shown in Table 2. The external surface area of H-ZS-2 is about 45.9 m²/g, which is lower than that of the other two samples as well as the lowest microporous volume, which is due to the regular needle-shaped morphology. The H-ZN-1 has a large mesoporous volume of about 0.29 cm³/g, due to the aggregation of small flakes, which is consistent with the adsorption and desorption curves of nitrogen. The H-ZS-1 and H-ZN-1 have large microporous surface area, which is caused by relatively small crystal size and rough outer surface of the samples. As shown
in the Figure S1 and Table S1, the N\textsubscript{2} adsorption for before protonation, after Pt loading and after catalytic reaction of the samples also was performed. The BET surface area and micropore surface area of the same carriers under different conditions did not change significantly, which indicated that the texture properties of zeolites were mainly depend on the properties of zeolites.

Table S1. Basic properties of the different samples in the form of protonation.

| Samples | Surface Area (m\textsuperscript{2}/g) | Volume (cm\textsuperscript{3}/g) |
|---------|--------------------------------------|----------------------------------|
|         | \(S_{\text{BET}}\) | \(S_{\text{mic}}\) | \(S_{\text{ext}}\) | \(V_{\text{micr}}\) | \(V_{\text{mes}}\) |
| H-ZS-1  | 226.6                  | 168.6                          | 58.0                  | 0.07                 | 0.21                |
| H-ZS-2  | 204.2                  | 158.3                          | 45.9                  | 0.05                 | 0.20                |
| H-ZN-1  | 243.6                  | 169.2                          | 74.4                  | 0.07                 | 0.29                |

3.2. Acidity

The acid strength of different catalysts is determined by NH\textsubscript{3}-TPD. It can be seen from Figure 5, all the zeolites have two main peaks around 190 and 400 °C, presenting typical TPD curves, which are attributed to the desorption of NH\textsubscript{3} from the weak and strong acid centers, respectively. Generally, NH\textsubscript{3} has a large absorption force at the strong acid adsorption site, which requires high temperature for desorption. Herein, different samples have almost same desorption temperature for NH\textsubscript{3} molecular. Then, we tested the samples after Pt impregnation for NH\textsubscript{3}-TPD (Figure S2), and the results showed that the NH\textsubscript{3} desorption temperature was basically the same as the samples in the form of protonation.

![NH\textsubscript{3}-TPD profiles of the samples.](image)

Figure 5. NH\textsubscript{3}-TPD profiles of the samples.

The surface acidity of the catalyst has an important influence on the hydroisomerization of alkane. Figure 6 shows the hydroxyl properties of ZSM-23 zeolites by FT-IR spectra. The vibration region of infrared hydroxyl group is 3800–3300 cm\textsuperscript{-1}, and the infrared peak at 3745 cm\textsuperscript{-1} belongs to the isolated silicon hydroxyl group on the outer surface of the sample [22]. The infrared peak at 3735 cm\textsuperscript{-1} belongs to the silicon hydroxyl group in the ZSM-23 micropores [22,23]. The broad peak at the center of 3500 cm\textsuperscript{-1} belongs to the nested silica hydroxyl group, and the hydroxyl group bridged by aluminum silicate appears at 3600 cm\textsuperscript{-1} [23], which is B acid. Usually the B acid sites of silica-aluminum zeolites
are supplied by hydroxyl groups bridging (Si-OH-Al) between silica and aluminum, and all samples have the same type of B acid, which is consistent with the same NH$_3$-TPD desorption temperature of the three zeolites described above.

![Figure 6. FT-IR spectra of different zeolites in the region of OH stretching.](image)

The IR spectrum of chemisorption of basic molecules has been widely used to determine the acidity of porous materials. The amount of B acid and Lewis acid (L acid) of the catalyst can be further measured by Py-IR. The total acid content of zeolites was calculated by pyridine desorption at 150 °C, and the strong acid content of the zeolites was calculated by desorption of pyridine at 350 °C (Figure 7 and Table 3). The bands at 1445–1460 and 1540–1548 cm$^{-1}$ are related to adsorption peaks of pyridine on L acid and B acid sites, respectively, while the adsorption peak of 1490 cm$^{-1}$ is caused by the interaction between B acid and L acid [24]. The H-ZS-2 contains the least L acid. While, the sample H-ZN-1 has the highest amount of B acid, which is due to its large microporous surface area higher aluminum content on the outer surface. To further clarify the catalytic mechanism, we performed Py-IR characterization of the impregnated catalyst. From Figure S3 and Table S2, we can see the content of the strong acid and weak acid for B acid and L acid was almost the same as the samples in the form of protonation.

![Figure 7. Infrared spectra of pyridine adsorbed on as-synthesized zeolites at 150 °C (a) and 350 °C (b).](image)
Table 3. Acidities of the zeolites determined by Py-IR.

| Samples  | Acidity Types (µmol/g) | 150 °C | 350 °C | 150 °C | 350 °C |
|----------|------------------------|--------|--------|--------|--------|
|          | Bronsted               | Lewis  |        |        |        |
| H-ZS-1   | 131                    | 26     | 18     |        |        |
| H-ZS-2   | 136                    | 100    | 11     |        |        |
| H-ZN-1   | 182                    | 137    | 24     |        |        |

Due to the small pore size of ZSM-23 zeolite, the isomerization reaction of long-chain alkanes is mainly carried out on the outer surface and pore mouth of ZSM-23 zeolite. Therefore, the surface acid properties of ZSM-23 zeolite have an important effect on its catalytic performance. The acid sites on the external surface can be determined by selecting the alkaline molecules with a molecular diameter larger than the pore size of zeolite. The kinetic diameter of 2,6-di-tert-butylpyridine (dTBPy) is 1.05 nm [25], and it cannot enter into the channels of the ZSM-23 (0.45 nm × 0.52 nm) zeolite, so the acidic sites on the zeolite surface can be studied by IR spectra of dTBPy. Figure 8 shows the infrared results of dTBPy desorption on different zeolites at 150 °C. The infrared peak at 1615 cm⁻¹ is due to the interaction between dTBPy and B acid located on the outer surface of the zeolites. The B acid on the outer surface of the samples is in the order of H-ZN-1 > H-ZS-1 > H-ZS-2, indicating that large external area exposes more acidic sites.

In addition to study the acid properties of the carrier, the noble metal Pt has an important effect on the hydroisomerization of the alkane. Pt with a content of 0.5 wt. % was loaded on all the samples. Figure 9 exhibits the TEM images of Pt dispersed on ZSM-23 zeolites, the Pt sizes shown here represent the size of most Pt particles over different samples, respectively. Pt/H-ZS-2 shows a maximum Pt particle size of about 2.5 nm, which may be due to its minimum external area and smooth external surface (Table 2). While the Pt particle size of about 1.9 nm of the Pt/H-ZN-1 can be attributed to the high B acid content and the rough outer surface of the sample (Table 1). The average size of Pt particle calculated by CO pulse adsorption is shown in Table 1. We can see that the particle size of Pt calculated is close to that observed by TEM. The order of B acid content on the outer surface of the zeolites is Pt/H-ZN-1 > Pt/H-ZS-1 > Pt/H-ZS-2, and the Pt particle size decreases in the order...
of Pt/H-ZN-1 > Pt/H-ZS-1 > Pt/H-ZS-2. Therefore, the dispersion and the size of Pt particles mainly depend on the B acid amount on the outer surface of the zeolites.

![Figure 9. TEM images of Pt loaded zeolites (a) Pt/H-ZS-1; (b) Pt/H-ZS-2; (c) Pt/H-ZN-1.](image)

In order to further study the effect of the surface properties of different zeolites on the properties of Pt particle, the reducibility of Pt over different catalysts was characterized by H$_2$-TPR. As shown in Figure 10, all the catalysts have two H$_2$ reduction peaks in the temperature range of 150 to 350 °C and one broad peak at 400–500 °C. The hydrogen reduction peaks at 200 °C of the catalysts are attributed to the reduction of PtO and PtO$_2$ species coordinated with the outer surface of zeolites [26]. And the broad peak at 400–500 °C is generally considered to be the Pt species that is difficult to be reduced over the catalyst because of the strong metal-support interaction [27]. Pt/H-ZS-1 and Pt/H-ZS-2 have similar hydrogen reduction peaks of Pt. However, the Pt/H-ZN-1 has a large reduction peak at a higher temperature of 275 °C due to its higher acid density and acid strength. The results show that the catalyst with aluminum sulfate is easy to be reduced. The results show that the catalyst with aluminum sulfate as aluminum source is easier to be reduced due to the weakening interaction between the metal and the zeolite.

![Figure 10. H$_2$-TPR curves of different samples.](image)
3.4. Catalytic Performance

At present, there is still much debate on the effective acidic sites in long-chain alkanes hydrogen isomerization. However, many studies have shown that [28] the branched chains formed in the hydroisomerization of long-chain alkanes cannot be carried out in the pores due to the diffusion limitation. Martens [29] and others further studied that the isomerization of long-chain alkanes mainly occurred on the surface of zeolite and the acidic sites near the pore, but could not occur in the zeolite pore. They also proposed the concept of “pore and key-lock” catalysis in alkane isomerization of microporous zeolites.

For the metal-acid bifunctional catalysts, it is recognized that alkanes are first adsorbed at the metal sites and dehydrogenated to form olefins, then the olefins diffuse to the acid sites for isomerization, and finally the iso-olefins intermediates diffuse to the metal site for hydrogenation reaction [30]. Thus, the balance between metals and acids is crucial to isomerization performance of alkanes [31].

In this paper, we use n-dodecane isomerization as the probe reaction to study the catalytic performance of zeolites. The results of the isomerization reaction of n-dodecane on different samples are shown in Figure 11. From these results, we can see that the conversion of all the catalysts increases gradually with the increase of reaction temperature (Figure 11a). Pt/H-ZS-1 with the strongest B acid sites showed the highest conversion of n-dodecane. In contrast, Pt/H-ZS-2 with the fewest B acid sites needs higher reaction temperature to reach the same conversion as Pt/H-ZS-1 and Pt/H-ZN-1 catalysts. The variation trend of i-dodecane selectivity on the catalysts with the reaction conversion is plotted in Figure 11b. With the increase of n-dodecane conversion, the i-dodecane selectivity of all catalysts decreases gradually, which is due to the fact that high temperature is favorable for cracking side reaction. When the reaction temperature is 271.5 °C, the n-dodecane conversion on the Pt/H-ZN-1 is 91.4% and the selectivity of i-dodecane is only 72.2%. This may be due to the H-ZN-1 carrier contains a large number of strong L acid and B acid, which enhance the cracking reaction. When the reaction temperature is 245.5 °C, the n-dodecane conversion on Pt/H-ZS-2 is 36.8%, and the selectivity of the i-dodecane is 89.7%, which is due to its Low B acid strength and low L acid content, and L acids can cause cracking of alkanes. When the reaction temperature rises to 275.8 °C, the conversion of n-dodecane is 90.4%, while the selectivity of i-dodecane is decreased to 79.5%. This may be because the low dispersion and large particle size of Pt on the Pt/H-ZS-2, providing fewer metal sites, which makes the de/hydrogenation and isomerization reactions mismatched [32]. Under the condition of high conversion, the olefin intermediates cannot be hydrogenated at the metal center in time, resulting in a decrease of catalyst activity and isomer selectivity. However, at the reaction temperature of 274.4 °C, the n-dodecane conversion of Pt/H-ZS-1 is 90.7%, and the i-dodecane selectivity is 81.2%. Obviously, Pt/H-ZS-1 exhibits higher stability and i-dodecane selectivity than the other two catalysts under high conversion conditions, which attributes to the suitable B acid and high Pt dispersion.

![Figure 11](image-url)  
**Figure 11.** Reaction results of n-dodecane isomerization on different samples: (a) n-dodecane conversion as a function of temperature, (b) i-dodecane selectivity versus conversion. (Reaction condition: H₂/n-dodecane = 750, LHSV = 1.2 h⁻¹, P = 4 MPa).
Martens et al. [33,34] showed that the shape-selective effect of zeolites results in linear alkanes being adsorbed in micropores (“pore mouth” adsorption) or both ends in adjacent micropores (“key-lock” adsorption). Claude et al. [34] further pointed out that the adsorption type of n-alkane on the microporous zeolites gradually changed from “pore mouth” adsorption to “key-lock” adsorption with the increase of reaction temperature. Accompanied by an increase in the n-dodecane conversion, the selectivity of the mono-branched isomers decreased gradually (Figure 12a); however, the selectivity of the multi-branched isomers increased gradually (Figure 12b). The selectivity of the mono-branched isomers on the Pt/H-ZS-2 decreases significantly following the increase of n-dodecane conversion, and when the conversion is greater than 81%, the selectivity of multi-branched isomers is higher than that of the other two catalysts. Due to the weak interaction between metal and the carrier and low Pt dispersion, the residence time of isomeric intermediates at the acid sites increase inevitably, which increases the possibility of further branching isomers. At the same time, the ratio of selectivity for mono-branched isomers to multi-branched isomers on different samples is depicted in Figure 12c. Which showed that there is the highest proportion of multi-branched isomers in i-dodecane products on Pt/H-ZS-1 under the same conversion. It is worth noting that the proportion of multi-branched products is relatively low at lower n-dodecane conversion on Pt/H-ZS-2, but when the n-dodecane conversion is higher than 85%, the proportion of multi-branched products is higher than on the Pt/H-ZS-1. This is largely because part of the olefin intermediates cannot be hydrogenated to alkanes at the metal center in time due to the low Pt dispersion on Pt/H-ZS-2 under the high conversion, and further were isomerized to multi-branched i-dodecane.

![Figure 12a](image1.png)  
**Figure 12a.** The selectivity of mono-branched isomers versus n-dodecane conversion on different catalysts. 

![Figure 12b](image2.png)  
**Figure 12b.** The selectivity of multi-branched isomers versus n-dodecane conversion on different catalysts. 

![Figure 12c](image3.png)  
**Figure 12c.** The ratio of multi-branched isomers to the mono-branched isomers versus n-dodecane conversion on different catalysts.
In order to study the influence of different acid distribution on the hydroisomerization of long-chain alkanes, the selectivity of cracked by-products and the distribution of several different isomers were analyzed under the condition of n-dodecane conversion of about 90%. The selectivity of cracked products against the carbon numbers distribution is plotted in Figure 13. On different catalysts, most of the cracked products account for a large proportion of linear alkanes, and the proportion of cracked isomers in the cracked products of the same carbon number increases with the increase of carbon number, which follow the type C $\beta$—cracking [35]. The distribution of cracked by-products is similar on Pt/H-ZS-1 and Pt/H-ZS-2 because of their similar acidic distribution, while the Pt/H-ZN-1 shows the highest cracking selectivity due to the more B acidity and L acid content of the carrier. Under the condition that the conversion rate of n-dodecane is about 90%, the distribution of several different i-dodecanes is analyzed, as shown in Table 4, the main branches of the mono-branched isomers are methyl. An increase in the reaction temperature corresponds to weak B acid sites and less Pt sites of Pt/H-ZS-2 because of their similar acidic distribution, while the Pt/H-ZS-1 shows the highest cracking selectivity due to the more B acidity and L acid content of the carrier. Under the condition that the conversion rate of n-dodecane is about 90%, the distribution of several different i-dodecanes is analyzed, as shown in Table 4, the main branches of the mono-branched isomers are methyl. An increase in the reaction temperature corresponds to weak B acid sites and less Pt sites of the Pt/H-ZS-2 leads to the enhancement of key-lock adsorption. Further, the selectivity of the intermediate branched isomers was improved and the second cracked reaction was inhibited. As a result, Pt/H-ZS-2 exhibits the highest selectivity for 4~6-Methylundecane and 2,4~9-Dimethylnonane. The secondary cracking reaction of Pt/H-ZN-1 is intensified by its strong and high B acid content, which shows the lowest selectivity of the multi-branched i-dodecanes.

![Figure 13](image)

**Figure 13.** Selectivity of cracked products with n-dodecane conversion of about 90% on different samples. (i) selectivity of cracked isomers; (i + n) selectivity of total cracked products. (Reaction condition: \(H_2/n\)-dodecane = 750, LHSV = 1.2 h\(^{-1}\), \(P = 4\) MPa).

**Table 4.** The distribution of isomerization products on different catalysts.

| Samples       | Pt/H-ZS-1  | Pt/H-ZS-2  | Pt/H-ZN-1  |
|---------------|------------|------------|------------|
| Temperature (°C) | 274.1      | 275.8      | 270.4      |
| Conversion (%)    | 90.7       | 90.4       | 90.5       |
| Selectivity (%)   | 81.24      | 79.51      | 75.48      |
| \(S_{MoB}/S_{MuB}\) | 7.11       | 6.86       | 9.52       |
| Distribution (%)  |            |            |            |
Table 4. Cont.

| Samples                  | Pt/H-ZS-1 | Pt/H-ZS-2 | Pt/H-ZN-1 |
|--------------------------|-----------|-----------|-----------|
| 2-3-Methylundecane       | 32.99     | 31.31     | 33.86     |
| 4-6-Methylundecane       | 36.20     | 37.69     | 32.51     |
| Methyl methylethynonane  | 1.57      | 1.20      | 1.16      |
| 3,8-Dimethyldecane       | 0.32      | 0.33      | 0.28      |
| 2,4-9-Dimethylmethane    | 8.10      | 6.93      | 5.58      |
| Others                   | 2.06      | 2.05      | 2.09      |

$S_{MoB}$ and $S_{MuB}$ correspond to the selectivity of mono-branded isomers and multi-branded isomers, respectively, at about 90% of conversion. 2-3-Methylundecane corresponds to the terminal branch chain isomers; 4-6-Methylundecane corresponds to the intermediate branched isomers.

4. Summary

ZSM-23 zeolites as-synthesized are considerable difference in acid distribution and Pt loading status over the zeolites. In the hydroisomerization of n-dodecane, the Pt/H-ZS-2 has the minimum external specific surface area and Pt dispersion, and Pt/H-ZN-1 has the maximum B acid amount and the strongest acid strength, both of which exhibit lower bi-branched isomerism selectivity and the highest cracking selectivity. The results indicate that the strong acidity of zeolite and the longer residence time of isomerization intermediates due to the low Pt dispersion are the important factors for the cracked reaction, which follow the type C $\beta$-cracking mechanism. The Pt/H-ZS-1 with suitable B-acidity and enough Pt sites, resulting in a good match between the acidic position and the metal position, exhibited the best isomerization performance for long-chain alkanes. The experimental results show that SO$_4^{2-}$ can promote the formation of zeolite crystals and improve the crystallinity of zeolites, while NO$_3^-$ facilitates the entry of Al into zeolite framework.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/10/21/7546/s1, Figure S1. N$_2$ adsorption-desorption isotherms for ZS-1 (a), ZS-2 (b) and ZN-1 (c) at different states, Figure S2. NH$_3$-TPD profiles of the samples after impregnation, Figure S3. Infrared spectra of pyridine adsorbed on as-synthesized zeolites at 150 °C (a) and 350 °C (b) after impregnation, Table S1. Basic properties of the different samples, Table S2. Acidities of the zeolites determined by Py-IR after impregnation.

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