Formation and Regeneration of Shape-Selective ZSM-35 Catalysts for \( n \)-Butene Skeletal Isomerization to Isobutene

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ABSTRACT: Skeletal isomerization of \( n \)-butene to isobutene was performed over formed ZSM-35 zeolites in a lab-scale, fixed-bed reactor. The formation conditions to produce isobutene with zeolites were varied to determine the most advantageous binding agent (pseudo-boehmite) amount and steam dealumination conditions. The optimal binding agent amount was 20 wt %. Steam dealumination stabilized the catalysts and enhanced the catalytic performance because of the stable Si/Al framework and suitable acidity. The optimized process conditions involved a reaction temperature of 410 °C, a weight hourly space velocity of 5 h\(^{-1}\), and an \( n \)-butene concentration in feedstock of 50%. After being on-stream for 296 h, the catalysts were stable and were able to be regenerated with a comparable catalytic performance. An isobutene yield of 33–43 wt % was achieved, and the selectivity of isobutene was higher than 90% after the reaction was carried out for longer than 15 h. Carbon deposition modified the pore structure to enhance the selectivity of isobutene because of the selective shape effect. This study shows promising results for future industrialization of the skeletal isomerization of \( n \)-butene to isobutene in the presence of optimized ZSM-35 catalysts.

INTRODUCTION

Isobutene is an important organic chemical material used in the production of methyl tertiary butyl ether (MTBE), tertiary butanol, methyl methacrylate, butyl rubber, and other highly valued chemicals. Currently, the major conversion pathways for the production of isobutene include the skeletal isomerization of \( n \)-butene, dehydrogenation of isobutane, and isomerization dehydrogenation of \( n \)-butane. \(^5\) The skeletal isomerization of \( n \)-butene has obtained increased attention to produce MTBE and other highly valued products. This technology also enhances the utilization of C4 and increases the supply of isobutene. The skeletal isomerization of \( n \)-butene is dependent on the acid catalysis technology. Researchers have developed Al\(_2\)O\(_3\)-based catalysts and various types of zeolites used in the skeletal isomerization of \( n \)-butene. \(^5\) Al\(_2\)O\(_3\)-based catalysts have been applied in the early stage of isomerization; however, this technology has been gradually replaced because of low catalytic activity and poor stability. Ferrierite \(^5\) has been heavily researched and utilized because of the special pore structure and size to selectively produce isobutene. In addition, ferrierite is becoming an attractive catalyst to use in the industry because of its strong carbon tolerance. \(^4\) Ferrierite catalysis occurs over a lifetime of hundreds of hours, and this type of material is included but not limited to SAPO-11, MCM-22/49, ZSM-5, ZSM-35, and ZSM-22/23. \(^6–7\) Promising catalytic activity has been achieved, especially with the ten-membered ring (MR) zeolite ZSM-35. \(^8–9\)

Properties such as acid strength (weak and strong), Bronsted (B) or Lewis (L) acid type, and active site distribution have a serious effect on the catalytic performance of the zeolite. \(^10–13\) The acid strength required for acid-catalyzed isomerization reactions can be ranked as the following: cracking \(\approx\) oligomerization > skeletal isomerization > double-bond shift and cis–trans isomerism. \(^5,14,15\) Moreover, the isolated acid sites reduce the number of side reactions. \(^16–18\) The acidity of zeolites can be adjusted by changing the Si/Al ratio, replacing alumina in the framework with other elements, or modifying the preparation/forming process.

Carbon deposition is an inevitable process in the skeletal isomerization of \( n \)-butene to isobutene. A small amount of carbon deposition enhances the selectivity, but too much carbon deposition leads to the deactivation of the cata-

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Wattanakit et al. studied the effects of various reaction times on carbon deposition. The carbon mainly blocked the 8-MR pore channel, but only a small amount of carbon was deposited on the 10-MR pore channel in the initial stage of the reaction. As the reaction continued, the 8-MR pore channel was blocked completely, whereas the 10-MR pore channel only had a slight amount of carbon deposition. Therefore, the catalyst could retain a high catalytic performance over a long period of time. The proper reactor type and reaction conditions reduce coke deposition on the catalyst. Modification of the catalyst components or structure also has the potential to reduce coking. Regeneration of catalysts can enhance the comprehensive economic benefits of industrial catalytic devices, reduce the consumption of catalysts, and protect the environment. The regeneration approach relates to deactivation reasons. Carbon deposition involves the physical coverage of the catalyst without any destruction of the structure of the catalysts. Therefore, combustion of the carbon on the catalyst or steam regeneration can be used to remove carbon deposition.

Although ZSM-35 has been applied as an isomerization catalyst, there is not a well-defined relationship between the catalytic performance and the active sites on the zeolite. There is also not a well-defined relationship between carbon deposition and catalyst stability because of limited characterization technologies. The objective of this study was to optimize the forming process to prepare superior catalysts in terms of the pseudo-boehmite binder amount and steam dealumination. This study also seeks to determine the reaction process conditions most conducive to maximize isobutene yield in terms of the reaction temperature, feedstock concentration, and weight hourly space velocity (WHSV).

Furthermore, coke deposition and catalyst regeneration were also investigated.

## RESULTS AND DISCUSSION

### Characterization of the Synthesized ZSM-35 Zeolite Powder

Scanning electron microscopy (SEM) images (Figure 1a) clearly showed that the synthesized ZSM-35 zeolite powder were present as rectangular shapes and had a sheetlike morphology. The particle size was relatively uniform. The X-ray diffraction (XRD) pattern of the synthesized ZSM-35 zeolite (Figure 1b) only had characteristic diffraction peaks at 2θ = 9.4°, 22.4°, 22.7°, 23.3°, 23.7°, 24.5°, and 25.3°, indicating that the synthesized ZSM-35 zeolites were well-crystallized and pure. The surface area and pore volume measured by N2 adsorption–desorption (Table 1) revealed that the synthesized ZSM-35 zeolite possessed a large surface area of 327.5 m²/g, and the pore volume was 0.157 mL/g. These results can be attributed to the small zeolite grains that were well-crystallized. The acid strength and type of the synthesized ZSM-35 zeolite were analyzed by temperature-programmed desorption of ammonia (NH3-TPD) and Py-infrared (IR), respectively. NH3-TPD profiles (Figure 1c) indicated that the synthesized ZSM-35 had two acid types, namely weak acid and strong acid, located at 100–200 and 200–350 °C.

![Figure 1. Synthesized ZSM-35 zeolite powder. (a) SEM image, (b) XRD pattern, (c) NH3-TPD profile, and (d) Py-IR profiles at the desorption temperatures of 200 and 350 °C.](image)

### Table 1. N2 Adsorption–Desorption Analysis of the Synthesized ZSM-35 Zeolite Powder

| Catalysts  | BET surface area, m²/g | BJH V_p, mL/g | t-microspore V_p, mL/g | D nm  |
|------------|------------------------|---------------|------------------------|------|
| synthesized ZSM-35 | 327.5 | 0.157 | 0.140 | 0.54 |
300–500 °C, respectively. Py-IR spectra of pyridine adsorption at 200 and 350 °C (Figure 1d) inferred that the synthesized zeolite had a large amount of Bronsted acidic sites (B) and a small amount of Lewis acidic sites (L) located at 1450 and 1450 cm⁻¹, respectively (Table 2).

Table 2. Bronsted (B) and Lewis (L) Acidic Site Distribution of the Synthesized ZSM-35 Zeolite Powder Analyzed by Py-IR

| Catalyst       | 200 °C, µmol/g | 350 °C, µmol/g | L/B | L/B |
|----------------|---------------|---------------|-----|-----|
| synthesized ZSM-35 | 0.432         | 1.284         | 0.048 | 1.134 |
|                | 0.337         | 0.042         |      |  

Optimization of the Forming Process for ZSM-35 Catalysts. The forming of the catalysts is important for catalytic performance and for the stability of the catalysts in the industry. In this study, the amount of the pseudo-boehmite binder and the steam dealumination were selected to be studied. All catalytic reactions in the formation were performed under reaction conditions, T = 410 °C, P = 0.1 MPa, WGS = 5 h⁻¹, and n-butene concentration = 50%. Details of the feedstock components are listed in Table S1.

Effects of the Pseudo-Boehmite Binder Amount on the Formed ZSM-35 Catalysts. The binder was applied to increase the bond strength between material particles to improve adhesion. In this study, pseudo-boehmite was chosen as the binder to investigate the shaped catalysts’ strength and catalytic performance. The results (Table 3) showed that the crushing strength of the catalyst increased as the binder amount increased from 0 to 40 wt %. NH₃-TPD profiles (Figure 2a) indicated that the catalysts had an increase in acidity as the binder amount increased from 0 to 20 wt %. However, when the binder amount increased from 20 to 20 wt %, the desorption peak area showed a reverse effect and the weak acidic sites decreased to an amount even lower than that of the Cat.-0. The reason for the decreased acidity was attributed to surface hydroxyl condensation, which took place during the molding and calcination processes. Py-IR spectroscopy (Figure 2b and Table 4) inferred that the total Lewis acidic sites (L) located at 1450 cm⁻¹ increased from 0.1 to 0.45 µmol/g as the binder percentage increased from 0 to 40 wt %. However, Bronsted acidic sites (B) located at 1540 cm⁻¹ exhibited the opposite tendency and decreased as the binder amount increased, as shown in Table 4. The L/B ratios at weak and strong acidic sites increased as the binder amount increased.

Catalytic performance results (Figure 2c,d) indicated that the conversion of n-butene and the yield of isobutene increased as the binder amount increased from 0 to 20 wt %. However, the continuous increase of the binder amount to 40 wt % led to the decrease of n-butene conversion and isobutene yield. This result is consistent with the NH₃-TPD and Py-IR results, indicating that the conversion of n-butene was related to the acidity of the catalyst. The selectivity of isobutene increased as the amount of binder increased from 0 to 40 wt %. This may have occurred because Al₂O₃ deposited on the inner pores of the structured zeolites decreased the size of the channels, which favored a single molecule reaction. Therefore, the optimal binder amount was 20 wt % to generate isobutene.

Effect of Steam Dealumination on Formed ZSM-35 Catalysts. Hydrothermal treatment is an effective approach to enhance the stability of the catalyst and the selectivity of the desired products by adjusting the acidity and structure of the catalyst.²⁶ In this study, the formed ZSM-35 with 20 wt % pseudo-boehmite binder was selected for hydrothermal treatment. NH₃-TPD profiles (Figure 3a) indicated that the weak acidic site amount did not change, whereas the strong acidic sites decreased slightly. However, the Py-IR spectra (Figure 3b and Table 5) inferred that the B acid type amount decreased substantially after hydrothermal treatment, whereas the L acid type amount increased largely. The solid-state nuclear magnetic resonance (NMR) spectra²⁹Si of the hydrothermal and nonhydrothermal treatment are shown in Figure 3c. The shift of approximately −100.2419 ppm was assigned to Q(2Al); the shift of approximately −105.3952 and −108.6855 ppm were assigned to Q(1Al); the shift of −112.0363, −114.7540, and −116.4758 ppm were characterized as Q(0Al).²⁶,²⁷ The calculated framework Si/Al molar ratio for the nonhydrothermal and hydrothermal treated catalysts were 56.50 and 84.90 using the following equation, respectively, indicating that the framework Al atoms were partly removed. The removed framework Al atoms were responsible for the decreased B acid type amount and the increased L/B ratio, which was consistent with the reported work.²⁷

\[
\frac{n_{Si}}{n_{Al}} = \frac{4}{\sum_{n=0}^{4} I_{Si(nAl)}} + \frac{4}{\sum_{n=0}^{4} 0.25 n I_{Si(nAl)}}
\]

The catalytic performance results (Figure 3d,e) indicated that the conversion of n-butene in the presence of hydrothermal-treated catalysts was always higher than that of the fresh catalysts during the isomerization reaction. The hydrothermal-treated catalysts showed less isobutene selectivity in the first 40 h but reached the same level in the later 60 h. Moreover, the hydrothermal-treated catalyst showed only a slightly lower yield of isobutene during the first 20 h; however, it had a higher and stable isobutene yield after 40 h. These results implied that the hydrothermal treatment enhanced the stability of the zeolite by removing the active sites responsible for catalyzing oligomerization and cracking reactions.²⁸ The decreased strong acidic sites in NH₃-TPD results supported this conclusion, which led to coking and catalyst deactivation. The slight increased yield of propene was possibly due to the increased L acidic type, which was the active site for catalytic cracking. Another reason was possibly because the secondary pore was formed during hydrothermal treatment, which was beneficial for molecular diffusion and cracking of low polyolefin.

Optimization of Skeletal Isomerization Process Conditions. The process conditions such as the reaction temperature, n-butene concentration, and WHSV have significant effects on the isomerization process.²⁹ Therefore, these three parameters have been systematically investigated in this work. Reaction temperature studies (Figure 4a,b) indicated that the conversion of n-butene, the selectivity of isobutene, and the yield of isobutene all increased as the
The reaction temperature increased from 350 to 410 °C. However, the conversion of n-butene decreased, whereas the selectivity and yield of isobutene increased slightly when the temperature was continuously increased to 450 °C. The yield of heavy components (C5+) increased slightly and that of propene substantially increased as the temperature increased from 350 to 450 °C. The decrease of n-butene conversion was probably due to side reactions that occurred, involving cracking and coking of polymerized products at high reaction temperatures. The selectivity of isobutene increased because of the channel modification from carbon deposition and the interaction between kinetics and thermodynamics.29,30 Considering the catalyst stability and low byproduct production, the optimal temperature for the isomerization reaction was 410 °C.

The n-butene concentration study (Figure 4c,d) inferred that the conversion of n-butene and the yield of isobutene increased slightly even though the selectivity increased slightly as the n-butene concentration increased. The yield of C5+ increased, but the yield of propene decreased. The high concentration of the precursor feedstock increased the partial pressure of n-butene, which was beneficial for the oligomerization of olefins; however, the increased concentration decreased the contact frequency between n-butene and the active sites on the catalyst, which resulted in an insufficient reaction. Generally, the initial reaction stage involved the bimolecular mechanism.8 As the concentration of n-butene increased, the yield of C5+ increased because the less contact frequency increased the amount of unreacted biopolymers. Moreover, the higher n-butene concentration was beneficial for dimerization to produce more carbon, which modified the pore channel by covering the strong acid sites; therefore, the selectivity of isobutene increased. The catalysts have great adaptability to the concentration range of n-butylene; however, an extremely high concentration of n-butene resulted in a high yield of byproducts and rapid carbon deposition. Therefore, low concentrations of n-butene were most beneficial for favoring the isomerization reactions.

Generally, when the amount of catalyst loading is fixed, the device-processing capacity increased, but the contact time of raw material and catalyst was shortened with the increase of WHSV, which led to a decreased conversion degree of the raw material and the yield of isobutylene. On the contrary, the contact time of the material and the catalyst was prolonged, but the byproduct increased and the selectivity of isobutene decreased with the decrease of WHSV. The n-butene conversion and yield of isobutene decreased with the increase of WHSV. The reason for this was because the contact efficiency between n-butene and the catalyst active sites decreased as the WHSV increased. In addition, the short contact time decreased the possibility of occurrence of polymerization reactions.31 Therefore, although the conversion of n-butylene and the yield of isobutylene are high when the WHSV is low, considering the selectivity and process capacity...
...of isobutylene, the optimal WHSV condition for the skeletal isomerization of \( n \)-butene was 5 h\(^{-1} \) (Figure 4e−g).

**Stability and Regeneration of ZSM-35 Catalysts.** The stability of the catalyst is a key factor for industrialization. Carbon deposition inactivation is an inevitable process, and the carbon type determined the regeneration process used on catalysts, which already underwent the reaction. During the initial reaction time of 20 h, the conversion of \( n \)-butene decreased rapidly from 60 to 45%, whereas the selectivity of isobutene increased from 55 to 90% (Figure 5a−c). This initial phenomenon matched the reported bimolecular mechanism, namely, the initial polymerized byproducts were deposited inside the pore channel. These byproducts covered the strong acid sites and modified the channels to increase the selectivity of isobutene. Therefore, the deposition of carbon played a vital role in shape-selective catalysis.\(^{32} \) As the reaction time on-stream continued, the conversion of \( n \)-butene, the selectivity of isobutene, and the yield of isobutene tended to be stable but slightly decreased over time. A yield of isobutene at 33−43 wt % was achieved, and the selectivity of isobutene was higher than 90% after the reaction was carried out for longer than 15 h, indicating that the ZSM-35 catalyst had excellent stability. These results are comparable to the industrialized skeletal isomerization to isobutene with an isobutene yield of 28.35−47.5 wt % in the presence of various types of catalysts.\(^{33,34} \) In addition, for long-time running of 30 days, the catalyst synthesized under optimal conditions exhibited a slightly higher yield of isobutene than the commercial catalyst purchased from Langdale, as shown in Table S2.

Compared to the fresh catalysts, the regenerated catalysts showed slightly lower \( n \)-butene conversion in the initial 50 h but a similar conversion as the reaction progressed over time. Isobutene selectivity and yield of the regenerated catalysts were slightly lower than those of fresh catalysts, whereas the propene yield only varied slightly during the initial reaction. These catalytic performances suggested that the regenerated catalysts did not recover completely, but their performances were like those of the fresh catalysts, indicating that the regeneration process was effective. During the first 50 h, the conversion and selectivity differed significantly because of the remaining carbon, altered pore structure, and new acidity level in the regenerated catalysts. This was verified by the following: temperature-programmed oxidation (TPO), \( \text{NH}_3 \)-TPD, \( \text{N}_2 \) adsorption−desorption, and Py-IR characterization.

**Table 5.** Bronsted (B) and Lewis (L) Acidic Site Distribution of the Nonhydrothermal- and Hydrothermal-Treated Zeolite

| items                                | 200 °C, µmol/g | 350 °C, µmol/g | 200 °C | 350 °C | L/B |
|--------------------------------------|----------------|----------------|--------|--------|-----|
| hydrothermal-treated ZSM-35 (SiO\(_2\)/Al\(_2\)O\(_3\) = 70) | 1.003           | 0.837          | 0.228  | 0.711  | 1.199 | 0.321 |
| nonhydrothermal-treated ZSM-35 (SiO\(_2\)/Al\(_2\)O\(_3\) = 70) | 0.482           | 0.897          | 0.187  | 0.871  | 0.538 | 0.215 |

...
adsorbed hydrocarbons and the carbon deposited on the catalyst surface area, whereas the peak at 670 °C was from the high polymer carbon (graphitelike structure). The similar peak areas at 670 °C for used catalyst-6 and used catalyst-200 and the much larger peak area at 470 °C for used catalyst-200 suggested that the high polymer carbon (graphitelike structure) was formed at the initial stage of the reaction, whereas the lower polymer carbon was produced as the

Figure 4. (a,b) Effect of reaction temperatures on the catalytic activity (reaction conditions: \( n \)-butene concentration = 50%, pressure = 0.1 MPa, and WHSV = 5 h\(^{-1} \)), (c,d) effect of \( n \)-butene concentration on the catalytic activity (reaction conditions: \( T = 410 \) °C, pressure = 0.1 MPa, and WHSV = 5 h\(^{-1} \)), and (e–g) effect of WHSV on the catalytic activity (reaction conditions: \( n \)-butene concentration = 50%, pressure = 0.1 MPa, and \( T = 410 \) °C). The detailed component concentration in the feedstock is listed in Table S1.
reaction time increased. The remaining carbon or the interaction between the carbon and the zeolite may be one of the reasons for the improved selectivity.

$\text{N}_2$ adsorption–desorption analysis results listed in Table 6 show that the surface area for used catalyst-6 and used catalyst-200 decreased dramatically and the pore size increased largely compared to the fresh catalyst. The longer the reaction time, the more obvious change of the surface area and the pore structure. The surface area decrease could be due to the blockage of the small size pores, indicating that the carbon deposition occurred within the 8-rings, followed by the 10-rings. Moreover, the deposited carbon may have formed macromolecular substances, which resulted in the increase of the pore size. The decreased surface area and the enlarged pore size in the regenerated catalyst further demonstrated that the catalysts have not been entirely rejuvenated, which further proved that the carbon deposition in the initial stage of the reaction cannot be combusted completely because of the higher polymerization degree and the larger graphitization degree. These results agreed with the TPO analysis results.

NH$_3$-TPD analysis results (Figure 5e) indicated that there were two types of acid sites, including $100–200 ^\circ \text{C}$ for weak acid sites and $350–450 ^\circ \text{C}$ for strong acid sites. Compared to the fresh catalysts, both the weak and strong acid sites decreased dramatically for used catalyst-6 and used catalyst-200. There were almost no strong acid sites on the used catalysts. For different reaction times, the strong acid sites decreased to the same degree, but the weak acid sites decreased as the reaction time increased. This showed that the strong acid sites were covered by carbon before the weak acid sites. The active sites for the isomerization were primarily}

**Table 6. N$_2$ Adsorption–Desorption Analysis of Fresh, Used, and Regenerated Catalysts**

| item             | fresh catalyst | used catalyst-6 | used catalyst-200 | regenerated catalyst |
|------------------|----------------|-----------------|-------------------|---------------------|
| surface area ($\text{m}^2\text{g}^{-1}$) | 323.4          | 59.75           | 35.8              | 260.1               |
| pore volume ($\text{cm}^3\text{g}^{-1}$) | 0.1501         | 0.1699          | 0.1612            | 0.1595              |
| average pore size/\text{nm} | 0.55           | 1.9             | 3.03              | 0.64                |
due to the weak acid sites because the selectivity of the isobutene increased with the time-on-stream.\textsuperscript{34} For the regenerated catalyst, the strong acid site amount decreased, inferring that there was remaining carbon, which covered the active sites in the regenerated catalysts. Because of the high amount of carbon deposition, it was impossible to characterize the used catalysts by Py-IR. Therefore, only fresh and regenerated catalysts were characterized by Py-IR (Figure S5), where 1540 cm\textsuperscript{-1} was assigned to the B acid type and 1450 cm\textsuperscript{-1} was attributed to the L type. The Py-IR spectra indicated that the B acid type did not recover completely, whereas the L acid types were similar when compared to the fresh catalyst. Py-IR aligned well with the NH\textsubscript{3}-TPD results and showed that part of the deposited carbon remained strong in the B acid type, which corresponds well to the N\textsubscript{2} adsorption/desorption and TPO results. This important discovery indicated that the carbon deposition could be adjusted by acid type and acid distribution.\textsuperscript{37,38}

## CONCLUSIONS

ZSM-35 catalysts were synthesized via a hydrothermal method and then formed for isomerization catalytic reaction. The amount of acidity strength and the type of formed ZSM-35 catalysts can be adjusted by adjusting the binder amount and hydrothermal treatment to maximize the production of isobutene. Taking the process capacity and economic performance of chemical companies into consideration, the optimized reaction conditions were 410 °C for the WHSV, and a 50% etherification C4 mixture concentration. In addition, the catalytic performance of the regenerated ZSM-35 catalysts after running 296 h was comparable to that of fresh catalysts, inferring that the regeneration process was excellent and effective. Coking enhanced the selectivity of isobutene because of the shape-selective reaction. This research is promising for the industrialization of the skeletal isomerization of n-butene to isobutene in the presence of formed and optimized ZSM-35 catalysts under optimal process conditions.

## EXPERIMENTAL SECTION

### Synthesis of ZSM-35 Zeolite Powder.

ZSM-35 with a high pure phase and crystallization degree was synthesized via a hydrothermal method under the following experimental conditions: SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} = 70, alkalinity = 0.06, crystallization temperature = 160 °C, and crystallization time = 64 h. Typically, 0.16 g of sodium metasilicate and 0.25 g of sodium hydroxide were dissolved in water for 30 min. Subsequently, 5.17 g of pyridine and 13.5 g of Ludox (30.07, wt %) were added and stirred for 30 min at room temperature. For current experimental conditions, the mole ratio of Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, Na\textsubscript{2}O, C\textsubscript{5}H\textsubscript{5}N, and H\textsubscript{2}O is 1:69.1:4.2:1. For the regenerated catalyst, the strong acid site amount decreased, characterized, and tested for activity, which is explained in the following part.

### Formation of ZSM-35 Catalysts.

To satisfy the industrial requirement, ZSM-35 was formed into a clover shape to afford an improved mechanical strength to the catalyst. During the shaping process, the binder pseudo-boehmite amount and steam dealumination were systematically investigated to determine the optimal conditions. The antircrush strength of the formed catalysts was measured by a particle strength tester (model YHKC-3A). Details of the forming process are discussed in the Supporting Information, and the schematic of the hydrothermal treatment is shown in Figure S1.

### Hydrothermal Treatment of the Catalyst.

Approximately, 15 g of 3–5 mm catalysts was loaded into the reactor and hydrothermally treated at 550 °C and 0.3 MPa for 1 h with a WGSH of 2 h\textsuperscript{-1}. The details of the process are described in the Supporting Information, and the schematic of the hydrothermal treatment is shown in Figure S2.

### Catalytic Reaction.

Skeletal isomerization of n-butene was carried out in a fixed-bed continuous reaction apparatus (Figure S3) loaded with approximately 5 g of 2–3 mm diameter catalyst. The conversion of n-butene was monitored by varying the catalyst formed under various conditions, reaction temperature, concentration of n-butene, and WHSV. The temperature of the reaction was controlled by a temperature control cabinet (590U, Xiamen Yu Electric Automation Technology Co., Ltd), and the pressure was kept at atmosphere pressure. Different feedstock concentrations were obtained from an etherification factory. The product was analyzed using an Agilent GC-2000 II equipped with a flame ionization detector and an Agilent-GS-Alumina capillary column (50 m × 0.532 mm). The n-butene conversion (X, wt %), isobutene selectivity (S\textsubscript{5}, %), isobutene yield (Y\textsubscript{p}, wt %), propylene yield (Y\textsubscript{p}, wt %), and heavy component of C\textsubscript{5}+ yield (Y\textsubscript{C5+}, wt %) were calculated according to eqs 1–5, respectively.

\[
X = \frac{M_{W_{0n}} - (M - P)w_{W_{0n}}}{M_{W_{0n}}}
\] (1)

\[
S_5 = \frac{(M - P)w_{W_{0n}} + Pw_{W_{0n}} - Mw_{W_{0n}}}{M_{W_{0n}} - (M - P)w_{W_{0n}}}
\] (2)

\[
Y_p = \frac{(M - P)w_{W_{0n}} + Pw_{W_{0n}} - Mw_{W_{0n}}}{M_{W_{0n}}}
\] (3)

\[
Y_{C5+} = \frac{(M - P)w_{W_{0n}} + Pw_{W_{0n}} - Mw_{W_{0n}}}{M_{W_{0n}}}
\] (5)

where M is the mass flow rate (kg/h), P is the recombinant flow rate (kg/h), and w is the mass fraction of the component (wt %). Subscript 0 represents the raw material, g represents the gaseous product (gas phase of production after condensation), l represents the liquid product (liquid phase of production after condensation), n represents n-butene, i represents isobutene, p represents propylene, and C\textsubscript{5}+ represents the heavy component including five carbons or greater hydrocarbon in the liquid product.
Regeneration of the Used Catalysts. The used catalysts were regenerated at a temperature of 330 °C first and then at 480 °C by burning the coke with 10% oxygen concentrations at a gas hourly space velocity of 2000 h⁻¹ and a pressure of 0.1 MPa. The effluent gas was analyzed via an Agilent GC2000 III analyzer. The regeneration process was completely finished when the CO₂ concentration in the effluent gas was lower than 0.04%.

Catalyst Characterization. The powder XRD patterns were carried out using a Bruker D8 ADVANCE X-ray diffractometer at 40 kV with a Cu Ka radiation source (λ = 1.5406 Å) at 2θ ranging from 5 and 50° with a step size of 0.02°. The diffraction lines were identified by matching them with reference patterns in the Joint Committee on Powder Diffraction Standards database.

N₂ adsorption/desorption isotherms at −196 °C were recorded using an ASAP2020M automatic surface ratio and aperture analyzer (U.S. Quantachrome). The samples were degassed in an N₂ flow at 90 °C for 1 h and were subsequently held at a temperature of 350 °C for 5 h before being measured. The specific surface area was calculated according to the Brunauer—Emmett—Teller (BET) method. The total pore volume was dependent on the adsorbed N₂ volume at a relative pressure of approximately 0.99. The micropore volume was obtained using the t-plotting method.

The morphology of these samples was investigated using a field emission scanning electron microscope (FEI, Quanta 200F) at an acceleration voltage of 40 kV and a current of 40 mA.

NH₃-TPD was carried out on an AutoChem II 2920 analyzer manufactured by Micromeritics (USA) to determine B acid and L acid concentrations using a QIC-20 mass spectrometer (British Hyde). A sample (0.1 g) was purged for 10 min under a He atmosphere, and then the temperature was increased to 800 °C at a heating rate of 10 °C/min with 10% O₂/He (50 mL/min). The signals of m/z = 18, 32, and 44 were detected by mass spectrometry.

Si magic-angle spinning NMR spectra were collected with a Bruker AVANCE III 500 MHz spectrometer at 130.327 MHz with a 0.9 μs pulse width, 6 μs delay time, and 12 kHz spinning speed.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00333.

Flow chart for forming ZSM-35 catalyst; schematic of the hydrothermal treatment of the catalysts; schematic of the continuous reactor for isomerization reaction; detailed information of the concentration of the feedstock; and comparison of the commercial and synthesized catalysts ZSM-35.

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Q.X. and Z.C. designed the experiments; W.Y. and Y.Y. carried out the experiments and characterizations; Y.L. and J.S. cowrote the paper; and Q.X., Z.C., H.Z. and C.X. analyzed the experimental data. All authors discussed the results.

Notes
The authors declare no competing financial interest.

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