

Article

Improvement of the Catalytic Efficiency of Butene Oligomerization Using Alkali Metal Hydroxide-Modified Hierarchical ZSM-5 Catalysts

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Abstract: Oligomerization of light olefin is an effective method to produce plentiful liquid fuels. However, oligomerization processes using microporous zeolites have severe problems due to steric hindrance. In this paper, oligomerization of butene using a series of new types of hierarchical HZSM-5 zeolite catalysts is studied. To obtain the modified HZSM-5 catalysts, HZSM-5 is treated with the same concentration of LiOH, NaOH, KOH, and CsOH aqueous solutions, respectively. It is demonstrated that the alkali treatment can effectively modify the acidity properties and hierarchical structure of the HZSM-5 catalyst, which is confirmed by X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Nitrogen Adsorption-desorption Measurements, Transmission Electron Microscopy Investigations (TEM), Ammonia Temperature-programmed Desorption Method (NH₃-TPD), Pyridine FT-IR, and Thermogravimetric Analysis (TGA). The results show that hierarchical catalysts with interconnected open-mesopores, smaller crystal size, and suitable acidity can better prolong the catalyst lifetime during butene oligomerization. Particularly, the HZSM-5 catalysts treated with CsOH aqueous solution (ATHZ5-Cs) proved to be the most effective catalyst, resulting in approximately 99% conversion of butene and exhibiting C₈⁺ selectivity of 85% within 12 h. Thus, an appropriate hierarchical catalyst can satisfy the oligomerization process and has the potential to be used as a substitute for the commercial ZSM-5 catalyst.

Keywords: hierarchical catalysts; alkali metal hydroxides; butene oligomerization; liquid fuel

1. Introduction

Light olefins are generally produced by catalytic cracking or dehydrogenation of light alkanes in the petro-chemical industry [1,2]. It is widely known that oligomerization of light olefins is an effective method to produce plentiful liquid fuels (such as gasoline and diesel) and specialty chemical intermediates (such as surfactants, plasticizers and elastomers) [3,4]. Light olefins are generally oligomerized by using homogeneous and heterogeneous catalysts. Therefore, research into catalysts is undoubtedly crucial for the development of oligomerization [5].

In the past years, most commercial oligomerization processes have been conducted by using homogeneous catalysts. However, the use of homogeneous catalysts causes many problems, such as the need for a complex purification process (generally, it is difficult to remove the homogeneous catalysts from products) and pollution [6]. Because of these issues, there is growing interest in the research into heterogeneous catalysts for oligomerization [7].

Butene, one of the most representative light olefins, is in surplus in the chemical industry [8]. Particularly, butene can not only be produced by Fischer–Tropsch synthesis and butane dehydrogenation but also derives from the biomass cracking and decarboxylation of carbohydrate-derived biomass γ -valerolactone [9–11]. Besides, methyl tertbutylether (MTBE) is prohibited in many countries, which also leads to a strong surplus of butene compared to ethylene and propylene [12]. In these circumstances, most refineries are facing the severe problem of a strong surplus of butene due to lower demand, which is an urgent problem that needs to be solved. One of the most effective ways to use the surplus butene is to transform the light olefins to liquid fuel by oligomerization. Until now, the commercial technology for butene oligomerization has made great progress using heterogeneous catalysts, especially, solid phosphoric acid (SPA) that is produced by the Universal Oil Products Company (UOP), which has been used as a commercial oligomerization catalyst for over 80 years. The generated liquid products are predominantly gasoline fractions produced through oligomerization using the catalyst [13,14]. However, SPA can easily be muddled and can contaminate the environment because of the presence of acid [15]. Worse still, the spent catalyst is non-recyclable during the process. Owing to the increasing awareness of environmental protection, environmentally friendly solid acid catalysts have drawn great attention. Among the numerous solid catalysts, zeolitic materials, which contain a unique pore structure and acid sites, are extensively studied because of their easier regenerability, lower environmental pollution issues, and the more flexibility of hydrocarbon product distribution [16]. Furthermore, zeolites have been widely used as solid acid catalysts in petroleum processes [17]. Numerous researches have been devoted to the study of the oligomerization of light olefins using zeolites and focused on the optimization of zeolites [18,19]. Particularly, among the conventional zeolites, H-ZSM-5 with three-dimensional medium pores and an intersecting channel system have been widely used [20]. Moreover, H-ZSM-5 (MFI topology) is considered as one of the most potential catalysts to replace phosphoric acid in the Mobil olefin to gasoline and distillate (MOGD) process [21,22].

Particularly, oligomerization of light olefins has been studied extensively over microporous zeolites [23–25]. However, the fatal drawback of microporous zeolites is their easy deactivation because the materials are connected with internal diffusion limitations. It is inferred that rapid catalyst deactivation is caused by the blocking of pores, which has a detrimental effect on the catalyst stability [26]. The progresses in mesoporous materials is sufficient to avoid diffusion limitations of zeolites [27,28]. Nevertheless, mesostructured solid acid catalysts exhibit lower hydrothermal stability and weaker acidity than those of the microporous zeolites, which strongly limit their applications in the petrochemical industry [29]. Recently, potential substitutes for the above-mentioned catalysts are composites that contain both micropores and mesopores (i.e., hierarchical porous catalysts). Interestingly, alkali treatment is found to be an efficient and easy method to generate mesopores and adjust the acidity within the zeolites. For example, Corma and coworkers studied the formation of mesopores in ZSM-5 through alkali treatment and used it for oligomerization of propene and pentene, which indicates that a synergistic effect between the hierarchical structure and acid site is crucial for obtaining an optimal catalyst (high conversion and good stability) [30]. Moreover, mesoporous mordenite prepared by alkali treatment proved to be highly stable and selective for oligomerization of pentene, and the mechanism of mesopore formation has been described in more detail [31]. The process includes roughening of the zeolite surface, and generation of new intracrystalline mesopores, followed by the fragmentation of crystals and even complete dissolution with increasing NaOH concentration. Subsequently, Wang et al. reported mesoporous ZSM-5 for ethylene oligomerization, and results showed that proper NaOH concentration of treatment of the HZSM-5 catalysts not only increases the liquid yield, but also improves the catalyst stability [32].

Recently, the self-condensation of propanal on zeolite catalysts treated with different alkali metals was clearly shown by Keller et al. [33]. They found that the catalysts treated with the aqueous alkali containing larger cations ($\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$) show higher catalytic activity for base-catalyzed applications. The phenomenon has also been observed by Dapsens et al. [34].

Dapsens et al. pointed that the desilication of ZSM-5 by hydroxides of different alkali metals led to the introduction of mesopores to different extents; they concluded that CsOH treatment was an efficient substitute for NaOH treatment for the introduction of selective Lewis acid site. However, there are no reports based on zeolite catalysts treated with different alkali metals for butene oligomerization. In the present work, We tried to obtain hierarchical porous H-ZSM-5 solid acid catalysts that were prepared by alkali treatment of H-ZSM-5 using LiOH, NaOH, KOH, and CsOH aqueous solutions, respectively; the hierarchical catalysts were further used for butene oligomerization. To the best of our knowledge, this is the first report on the treatment of H-ZSM-5 by different alkali metal hydroxides and their use for oligomerization. The objective of this study is to investigate the effects of different alkali metal hydroxides on ZSM-5 for butene oligomerization, thus attempting to obtain a best-performing catalyst with adequate hierarchical structure and acidic property for butene oligomerization, and further study its mechanism of mesopores formation through different alkali metals treatment. This study explores and provides a new method for the development of oligomerization using novel heterogeneous catalysts.

2. Results

The starting H-ZSM-5 zeolite with a nominal Si/Al ratio of 20 was named as HZ5. Hierarchical porous H-ZSM-5 catalysts were prepared by the alkali treatment of HZ5 using aqueous solutions of LiOH, NaOH, KOH, and CsOH in the same concentration (0.2 M), respectively. Please see the detailed preparation method of the facile alkali treatment procedure in the experiment part Section 3.1 (Catalyst preparation). The resulting solid powders are denoted as ATHZ5-Li, ATHZ5-Na, ATHZ5-K, and ATHZ5-Cs.

2.1. Characterization of Catalysts

2.1.1. X-ray Diffraction Analysis

The powder XRD profiles of the HZ5 catalyst and modified ATHZ5-Li, ATHZ5-Na, ATHZ5-K and ATHZ5-Cs catalysts are presented in Figure 1. All the characteristic diffractograms show that the structures correspond to the typical MFI crystalline phase, which indicates that the zeolitic character of the hierarchical catalysts is maintained even after the alkali treatment with LiOH, NaOH, KOH, and CsOH aqueous solutions. In addition, no new peaks were found in the profiles of all the modified catalysts, indicating that the hierarchical catalysts have no impurity phases. The intensities of the XRD reflections of ATHZ5-Li, ATHZ5-Na, ATHZ5-K, and ATHZ5-Cs catalysts are lower than those of the HZ5 catalyst. This implies that the relative crystallinity of the hierarchical catalysts decreased to some extent, possibly because of partial destruction of the zeolite crystal structure through the alkali treatment process. Previous researchers also reported the same trend [35,36]. Figure 1 shows that among the five catalysts, the ATHZ5-Cs catalyst has the lower relative crystallinity than that of the hierarchical catalysts.

2.1.2. X-ray Fluorescence Analysis

The Si/Al ratios of the catalysts were determined by XRF, and the data are presented in Table 1. The Si/Al ratios of the HZ5 catalyst significantly decreased after alkaline treatment, which indicates that the alkaline treatment can effectively remove the silicon species partially. This result is in agreement with reported results that alkaline treatment could remove the silicon inside the zeolite porous system more dramatically [37–39].

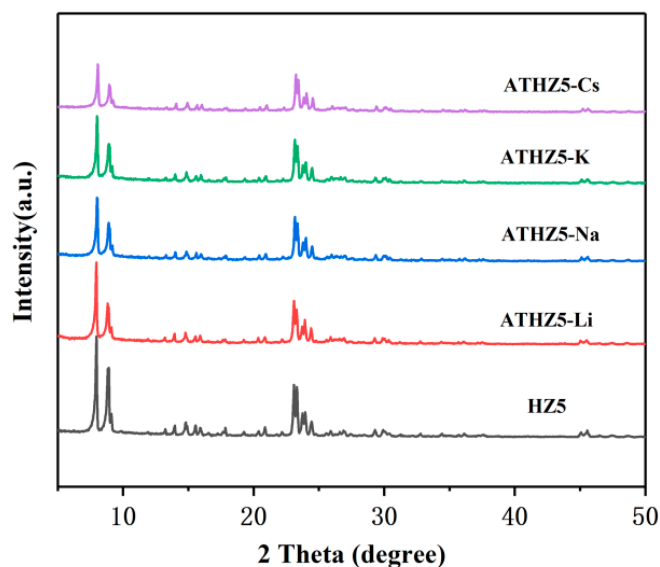


Figure 1. XRD profiles of HZ5 catalyst and modified catalysts. The modified catalysts were obtained by alkali treatment of LiOH, NaOH, KOH, and CsOH aqueous solutions, respectively.

Table 1. Elemental composition and textural properties of HZ5 catalyst and modified catalysts.

Catalyst	Si/Al ^a	S_{BET} (m^2/g) ^b	S_{micro} (m^2/g) ^c	S_{meso} (m^2/g) ^c	V_{Total} (cm^3/g)	V_{micro} (cm^3/g) ^c	V_{meso} (cm^3/g) ^d
HZ5	20.2	359.2	234.9	124.3	0.190	0.115	0.075
ATHZ5-Li	12.1	365.3	223.1	142.2	0.276	0.110	0.167
ATHZ5-Na	11.9	374.9	218.4	156.5	0.298	0.107	0.191
ATHZ5-K	11.8	373.1	223.8	149.3	0.286	0.109	0.177
ATHZ5-Cs	11.9	367.5	235.2	132.3	0.303	0.119	0.184

^a Si/Al ratio content: measured by XRF. ^b adsorption measurements (BET method). ^c adsorption measurements (t-plot). ^d adsorption measurements (Barret-Joyner-Halenda (BJH) method).

2.1.3. Porous Structure Characterization

The nitrogen adsorption–desorption isotherms of all the catalysts are presented in Figure 2a. The isotherms of the HZ5 catalyst exhibits a small hysteresis loops, implying that the HZ5 catalyst itself contains some mesopores. For the alkali-treated HZ5 catalysts, the nitrogen adsorption–desorption isotherms show obvious hysteresis loops over the p/p^0 range of 0.45–1.0, indicating a more effective development of mesoporosity after the alkali treatment using LiOH, NaOH, KOH, and CsOH, respectively. Moreover, the BJH pore size distribution curves of all the catalysts are presented in Figure 2b. The results show the appearance of a new peak centered at 4–7 nm for the alkali-treated catalysts, revealing a narrow size distribution of the mesopores in the materials. Therefore, it could be speculated that the modified catalysts contained both micropores and larger mesopores.

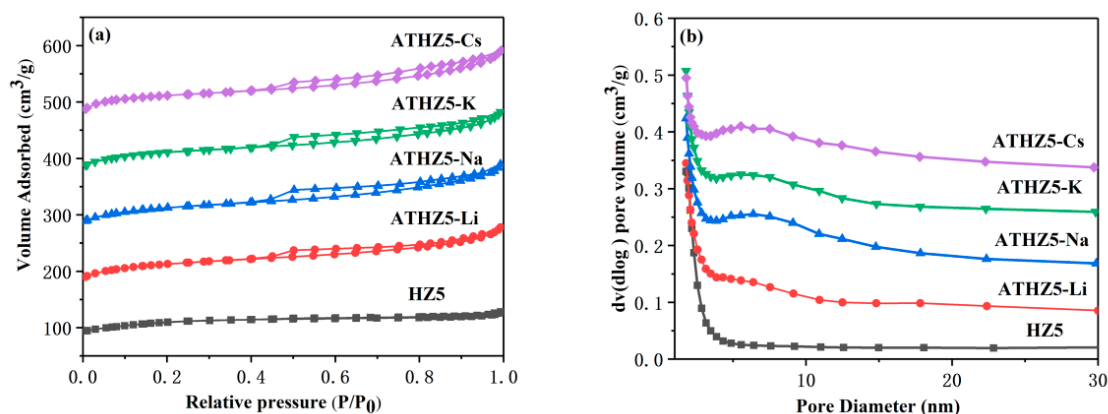


Figure 2. (a) Nitrogen adsorption–desorption isotherms and (b) Pore size distributions of HZ5 catalyst and modified catalysts.

The physical properties were further calculated using the BET and t-plot methods, respectively, as presented in Table 1. The HZ5 catalyst was treated by different alkali metal hydroxides, leading to an increase in the BET surface area and the total pore volume. In addition, Table 1 indicates that alkali treatment is an efficient method to create mesopores. As expected, the micropore surface area and volume decrease with corresponding increases in the mesopore surface area and volume of the HZ5 catalyst after the treatment of LiOH, NaOH, and KOH, which indicates that some of the micropores are destroyed and intracrystalline mesopores are formed. It is inferred that OH^- ions can easily attack the internal siloxane groups inside the ZSM-5 channels [40]. This can lead to the diffusion of many dissolved Si species out of the catalyst. Moreover, it can be seen that the mesopore surface area of the ATHZ5-Na catalyst is larger than that of the other catalysts, this is possibly because Na^+ can help balance the silicate anions in the NaOH solutions compared with other alkali cations [41]. For the ATHZ5-Cs catalyst, the BET surface area does not dramatically increase because the HZ5 catalyst undergoes more severe alkaline treatment (lower relative crystallinity, which is consistent with the XRD results), and its micropore surface area does not decrease (compared to HZ5 catalyst), possibly due to the fragmentation of crystals. The formation of new mesopores decreases because the intracrystalline mesopores are covered by crystal fragments, also in agreement with previous reports [31]. This result indicates that CsOH treatment is an effective and easy method to induce mesoporosity while maintaining the microporosity [34].

2.1.4. TEM Investigations

The TEM images of the HZ5 catalyst and modified catalysts are presented in Figure 3. The HZ5 catalyst contains a large amount of micropores (Figure 3a). Figure 3 demonstrates the successful formation of intracrystalline mesopores in the alkali-treated HZ5 catalysts. Particularly, the ATHZ5-Li catalyst maintains the morphology of the parent HZ5 catalyst (Figure 3b). Meanwhile, a large amount of intracrystalline mesopores is observed in the ATHZ5-Na catalyst (Figure 3c), along with a few disordered structures and slits. Moreover, etched pores of the ATHZ5-K catalyst were observed in the TEM image (Figure 3d) [42]. Furthermore, fragmentations of crystals of the ATHZ5-Cs catalyst can be seen (Figure 3e), indicating that the CsOH treatment can change the morphology of the catalyst. The TEM image of the ATHZ5-Cs catalyst indicates its smaller crystal size. Furthermore, the mesoporosity of the ATHZ5-Cs catalyst indicates that the CsOH-treated HZ5 possibly contains interconnected open-mesopores and closed mesopores, which is in agreement with the XRD results and data presented in Table 1.

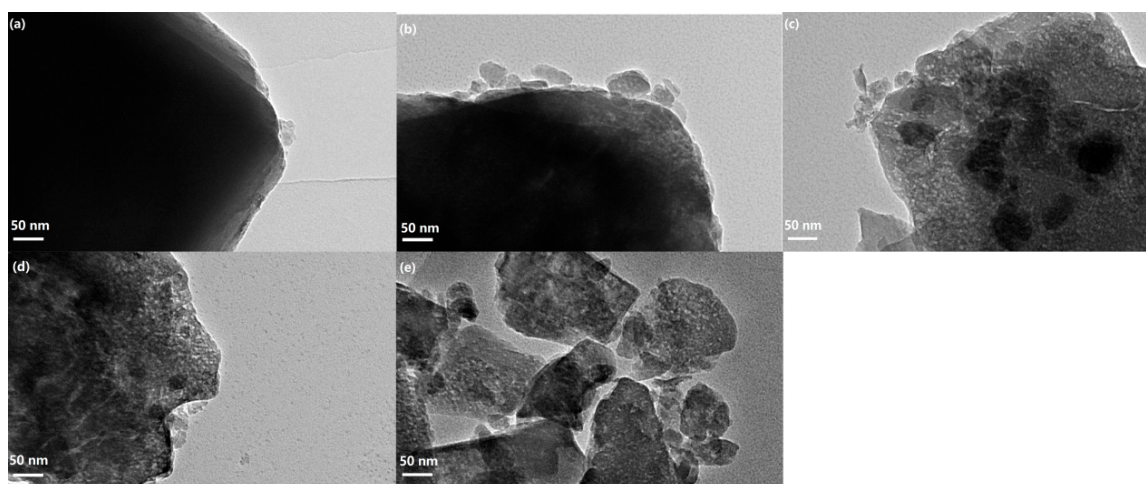


Figure 3. TEM micrographs of (a) HZ5 catalyst; (b) ATHZ5-Li catalyst; (c) ATHZ5-Na catalyst; (d) ATHZ5-K catalyst; and (e) ATHZ5-Cs catalyst.

2.1.5. NH_3 -TPD Analysis

The acidity of the catalysts was determined by NH_3 -TPD. Typically, the two peaks of the NH_3 -TPD profiles include a low-temperature peak (weak acid sites) at 110–275 °C and a high-temperature peak (strong acid sites) at 276–550 °C. As shown in Figure 4a, the two distinct desorption peaks of the alkali treated hierarchical catalysts (compared with HZ5) shifted toward higher temperatures, indicating an increase in the intensity of acid sites of the HZ5 catalyst after the treatment of LiOH, NaOH, KOH, and CsOH, respectively. It is implied that some acid sites, whether weak or strong, are newly added in the hierarchical catalysts. Since the amount of catalyst is the same in the NH_3 -TPD test, the peak area can be used to determine the amount of acid sites in the catalysts, the data are listed in Table 2 to provide an intuitive depiction. As seen in Table 2, in all the catalysts, the amount of strong acid sites is less than that of the weak acid sites, which is in agreement with a previous report (on microporous ZSM-5 with different Si/Al ratios) [43]. It is inferred that there is no direct relation between the Si/Al ratio and the amount of acid site. After the alkali treatment of HZ5 catalyst, the amount of acid site increase, which is also in agreement with previous reports [44–46]. The ATHZ5-Na catalyst has a higher total acid amount than that of the other catalysts, which can be attributed to the removal of Si and extra-framework Al species that deposit on the external zeolite surface [36,47]. The amount of acid sites in the hierarchical ATHZ5-Cs catalyst does not dramatically increase, which indicates that both amorphous Si and extra-framework Al species are partially removed after the CsOH treatment [46]. This further implied that the treatment of CsOH could significantly influence the porous structure of the microporous zeolite materials, which may explain the partial damage of the acid sites [48]. This is consistent with the TEM results.

2.1.6. Pyridine FT-IR Analysis

Figure 4b shows the type of acid sites of the HZ5 catalyst and modified catalysts. The calculated quantities of Brönsted and Lewis acid sites are displayed in Table 2. It is observed that all the catalysts display both Brönsted and Lewis acid sites. Compared with the HZ5 catalyst, the number of Lewis acid sites increases after treatment of the catalysts with LiOH, NaOH, KOH, and CsOH, respectively (Table 2). It should be noted that Lewis acid sites are generated due to the formation of extra-framework Al species, which is consistent with previous reports [49]. Notably, the ATHZ5-Na catalyst contains the highest amount of Brönsted acid sites, which can be attributed to the proper alkali treatment leading to higher Al content (i.e., a lower Si/Al ratio) [50]. However, after severe CsOH treatment, the highest L/B acid site ratio is generated in the hierarchical ATHZ5-Cs catalyst. Typically, Brönsted acid sites are

factors affecting the catalytic activity in oligomerization. More importantly, a high L/B acid site ratio was considered to improve the catalytic stability [51,52].

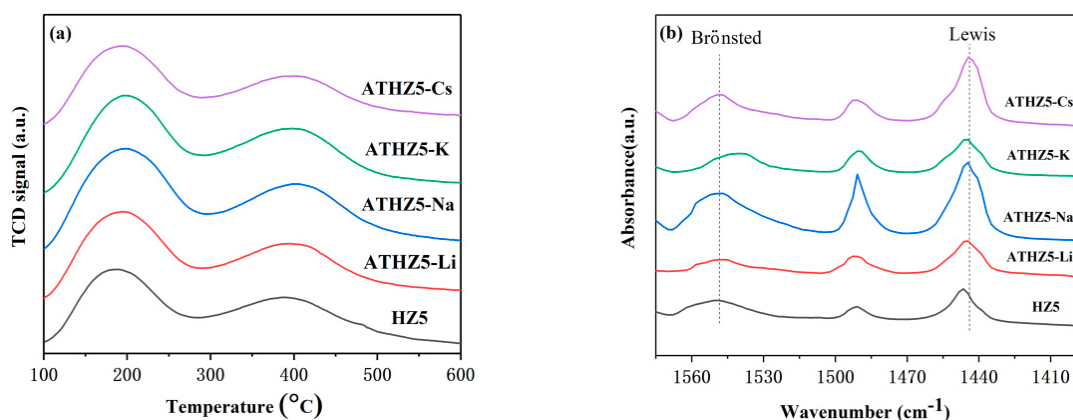


Figure 4. (a) NH_3 -TPD profiles and (b) Py-IR spectra of HZ5 catalyst and modified catalysts.

Table 2. Catalyst acidity results obtained by NH_3 -TPD and Py-IR.

Catalyst	Acidity by Strength ^a (mmol/g)			Acidity by Type ^b (mmol/g)		
	Weak	Strong	Total	Brønsted	Lewis	L/B Ratio ^c
HZ5	0.66	0.44	1.10	0.38	0.35	0.92
ATHZ5-Li	0.86	0.78	1.64	0.34	0.40	1.18
ATHZ5-Na	1.08	0.92	2.00	1.05	0.82	0.78
ATHZ5-K	0.94	0.91	1.85	0.4	0.41	1.03
ATHZ5-Cs	0.74	0.64	1.38	0.61	0.74	1.21

^a acidic strength measured by NH_3 -TPD. ^b Brønsted and Lewis acidity measured by pyridine FTIR adsorption.

^c Molar ratio of Lewis (L) to Brønsted (B) acid sites.

2.2. Catalytic Performance

The HZ5 catalyst and modified catalysts were investigated for butene oligomerization. The reaction mechanism for butene oligomerization is obey classical carbenium ion mechanisms [23]. Figure S1 illustrates the typical step of the Reaction scheme in butene oligomerization. According to a previous report [53], oligomerization of light olefins is a cascade reaction. Traditionally, butene derivatives, C_8 (octenes), are produced by dimerization, and C_8 can further react with surplus butene to produce largely hydrocarbons. This transient period has become a determining factor for the generation of oligomer products.

Based on the supplementary information (Figure S2), acidity is important for the oligomerization reaction [32]. However, the catalytic reactivity of all catalysts does not have a close relationship with the Brønsted acid sites. Thus, conversion of butene over the HZ5 catalyst and modified catalysts cannot be explained by the acid sites alone, which is also correlated with the diffusion limitation problem. Consequently, we concluded that the acid sites and the generated mesopores mainly contribute to the high activity of the liquid fuel. The liquid products obtained using the HZ5 catalyst and modified catalysts were analyzed by GC-FID (Gas Chromatography-Flame Ionization Detector) and followed the typical Schulz-Flory distribution (i.e., $\text{C}_8 > \text{C}_{12} > \text{C}_{16}$) [54]. Particularly, Figure 5 shows that the main products include dimers, trimers and some cracking olefins, mainly, C_3 – C_{11} hydrocarbons. These light olefins are produced by a secondary cracking reaction, which leads to the product distribution becoming broader. Besides lots of hydrocarbons products, there may still be paraffins, aromatics products via further hydrogenation, isomerization, or aromatization.

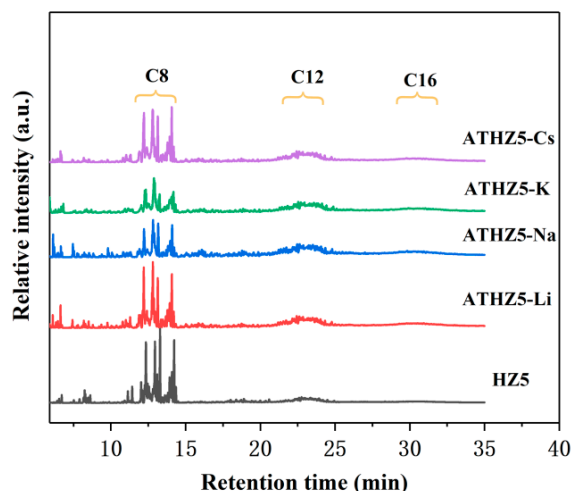


Figure 5. GC chromatograms of liquid products obtained after butene oligomerization at 473 K for 2 h on stream over HZ5 catalyst and modified catalysts.

Although some lighter products can be formed, the alkali treatment of HZ5 catalyst with LiOH, NaOH, KOH, and CsOH lead to higher yields of large carbon number olefins generated. Therefore, the products can likely be added to the gasoline/diesel pool and practically used as chemical intermediates.

Since butene oligomerization is an exothermic reaction, butene conversion by these catalysts increases with increasing reaction temperature [55]. Here, we studied the stability of all the catalysts for similar butene conversions after 2 h of reaction (Figure 6). As shown in Figure 6, butene conversion gradually declined with time on stream at 573 K due to coke deposition. For the HZ5 catalyst, butene conversion gradually decreases from 79.28% to 21.31% within 12 h on stream. This implies that heavier hydrocarbons are generated due to steric hindrance in the microporous zeolites. After treatment with LiOH, NaOH, KOH, and CsOH, respectively, the respective hierarchical catalysts displayed higher activity and greater stability for butene oligomerization.

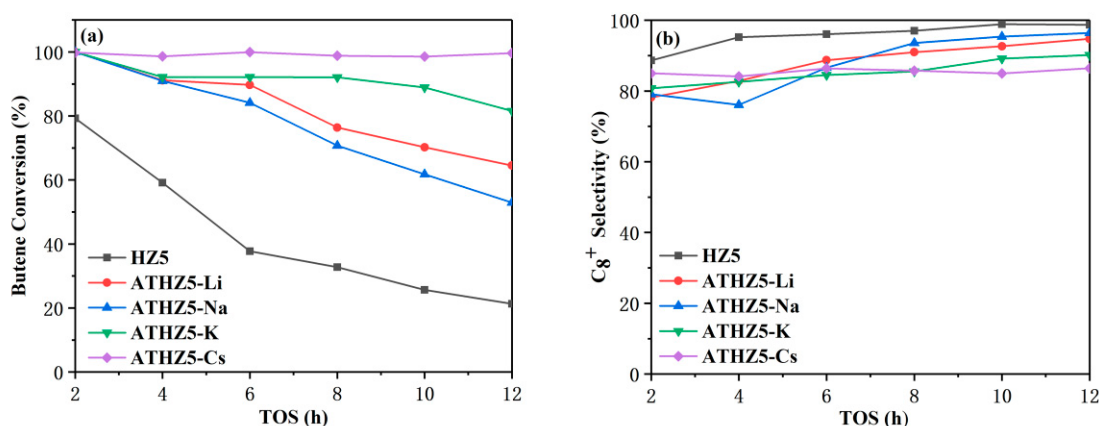


Figure 6. (a) Butene conversion and (b) C_8^+ selectivity of catalytic oligomerization of HZ5 catalyst and modified catalysts. Reaction condition: temperature 573 K, pressure 1.5 MPa.

Particularly, the ATHZ5-Na catalyst has a high amount of acid sites and a lower L/B ratio, which leads to a large amount of hydrocarbons, thus the hydrocarbons on the active sites of the catalyst are difficult to separate. These hydrocarbons further blocked the channels and destructed the acidic sites of the catalyst [56]. Thus, although there is a large amount of intracrystalline mesopores

in ATHZ5-Na, it still presents a faster deactivation. This is possibly because of not only the acid strength and acid type, but also the poor connectivity between the micropores and intracrystalline mesopores (closed mesoporous). Therefore, large amounts of hydrocarbons cannot easily diffuse out of the catalyst pores, (as confirmed by TEM).

In the catalytic conversion of butene, the ATHZ5-Cs catalyst shows the highest reaction stability among all the examined catalyst. Although butene conversion is slightly lower with less acid sites at 2 h, the activity remains unchanged until 12 h. Thereafter, the stability and stable activity of ATHZ5-Cs imply that the reactivity of C_8^+ oligomers is maintained. According to the BET results, the catalyst retains a large amount of micropores after the CsOH treatment and generated a moderate amount of intracrystalline mesopores inside the HZ5 crystallites. The TEM results further confirms the unique hierarchical structure of the ATHZ5-Cs catalyst possibly with interconnected open-mesopores and smaller crystal size, which provide shorter diffusion paths for olefins, thus effectively preserving the high catalytic activity. During the harsh alkali treatment, NH_3 -TPD shows that the amount of acid sites in the ATHZ5-Cs catalyst is slightly lower, which leads to small amounts of heavier hydrocarbons [57]. The ATHZ5-Cs catalyst with a higher L/B ratio can improve the catalyst stability, which is clearly shown by other researchers [27,58,59].

2.3. Thermogravimetric Analysis

Coke deposition indicates that deactivation is correlated with the formation of a large amount of heavier hydrocarbons. To illustrate catalyst deactivation, coke depositions of the different spent catalysts were tested in butene oligomerization at 573 K for 12 h (as detected in the TGA, Figure 7). Among all the catalysts, ATHZ5-Cs shows the lowest deposit carbon content, with the order of deposit carbon content being $ATHZ5-K < ATHZ5-Li < ATHZ5-Na < HZ5$. Catalyst deactivation is related to mesoporosity and acidity properties, which suggests that ATHZ5-Cs has a higher coke tolerance owing to the presence of shorter diffusion paths. Therefore, CsOH treatment of the HZ5 catalyst is more effective in restraining catalyst deactivation.

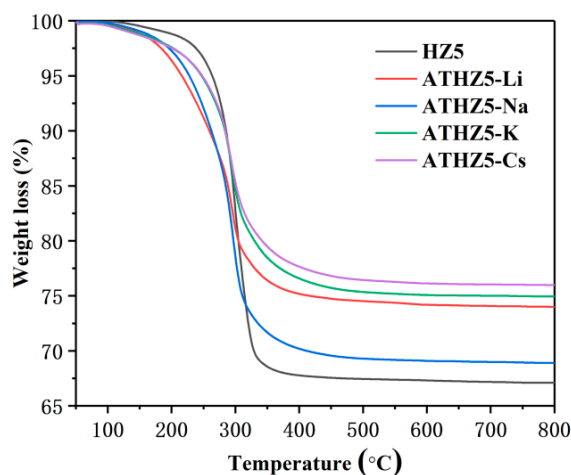
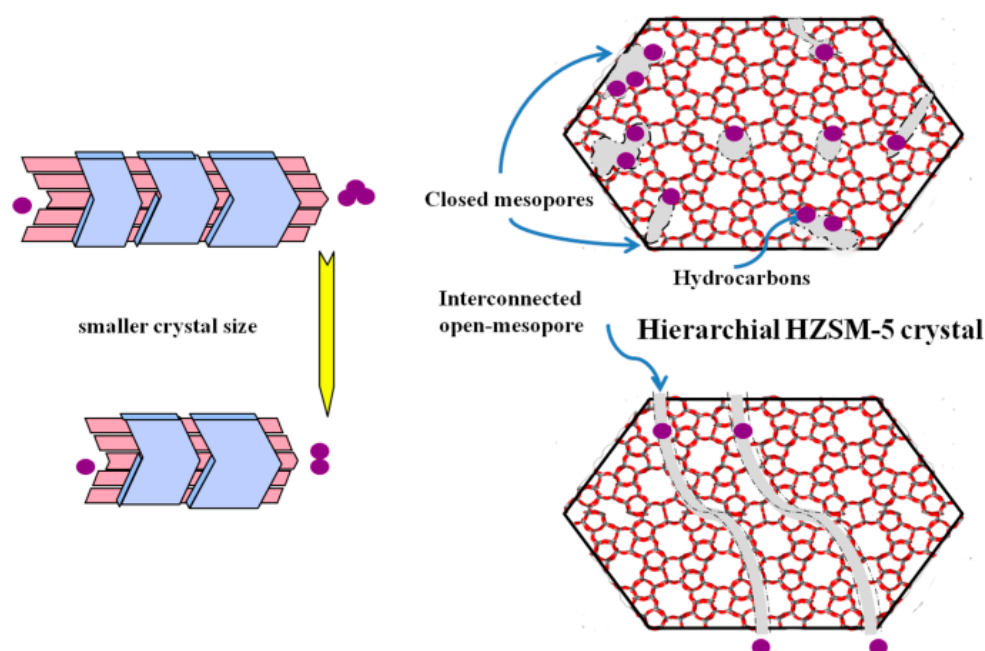


Figure 7. Thermogravimetric curves of spent catalysts after 12 h in oligomerization.

2.4. Schematic Illustration of the Improved Diffusion

To better understand the main mechanism of improved diffusion, it is schematically demonstrated in Scheme 1. Diffusion limitation within microporous zeolites is a severe problem because of fast deactivation. Above all, the CsOH-treated HZSM-5 catalyst was more resistant to deactivation through pore blockage compared to the commercial ZSM-5 catalyst. Apparently, compared with the closed intracrystalline mesopores, the interconnected open-mesopores are more effective in enhancing mass diffusion because the diffusion of large amounts of hydrocarbons out of the catalyst pores is favorable.

In addition, the crystal size is directly correlated with diffusion path lengths. Smaller crystallites in ATHZ5-Cs catalyst present a shorter diffusion path length, resulting in the formed oligomers would be able to egress the micropore structure quickly. Meanwhile, the shorter residence time in the pores is hardly favors secondary reactions. In this case, the probability to form undesired bulky hydrocarbons would be mostly reduced and hardly blocked the channels of the zeolite. The positive effect of shorter diffusion paths would be even more important when converting light olefins, due to their higher potential for formation of larger products, which could improve diffusion rate [60–62]. In conclusion, the unique hierarchical structure obviously promoted diffusion limitation inside the zeolite crystals. Furthermore, the interconnected open-mesopores, and the small crystal size contributed to the remarkably improved stability of the ATHZ5-Cs catalyst.



Scheme 1. Schematic illustration of the main mechanism of improved diffusion.

3. Materials and Methods

3.1. Catalyst Preparation

The HZ5 zeolite was provided by the Catalyst Plant of Nankai University (Tianjin, China). LiOH, NaOH, KOH, and CsOH were supplied from MACKLIN (AR) (Shanghai, China). The alkali treatment procedure was as follows: HZ5 was vigorously stirred at 85 °C for 90 min. Afterwards, the suspension was filtered and washed with double-distilled water until a pH of 7, and dried overnight at 100 °C. The samples were converted into the protonic form by ion exchange (1 M NH_4Cl , and 1 g of catalyst/20 mL of solution), and then again filtered, washed, and dried, as described above, followed by calcination at 550 °C for 4 h.

3.2. Catalyst Characterization

Powder XRD was performed using a Bruker D8 Advance X-ray diffractometer (BRUKER, Karlsruhe, Germany) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV, 30 mA), in the 2θ range of 5–50° with an angular step size of 4° min^{-1} . The bulk Si/Al ratio of the zeolites was analyzed using a Bruker S4 Pioneer X-ray fluorescence (XRF) spectrometer (BRUKER, Karlsruhe, Germany). Textural characterization of the materials was carried out by adsorption–desorption (−196 °C) experiments performed on a Micromeritics ASAP 2020 (Micromeritics, Norcross, GA, USA) to determine the

surface area and volume. Each sample was evacuated at 300 °C for 8 h under vacuum before the test, and Brunauer–Emmett–Teller (BET) surface area was evaluated from the nitrogen physical adsorption isotherms using the standard BET procedure. Transmission electron microscopy investigations were carried out on a JEM 2100 LaB6 FETEM microscope (JEOL, Tokyo, Japan). The acid property of the catalysts was determined by the ammonia temperature-programmed desorption method (NH₃-TPD) performed in He flow from 100 °C to 650 °C at a heating rate of 10 °C min^{−1} using a US Autosorb-1C-TCD-MS chemisorption analytical instrument. Pyridine FT-IR analysis were performed by using a US MAGNAIR-IR560 IR spectrometer (NICOLET, Madison, WI, USA). The amount of Brönsted and Lewis acid sites were calculated, based on the peak areas of 1540 cm^{−1} (Brönsted) and 1450 cm^{−1} (Lewis) bands [63]. The spectra were recorded at 423 K. Thermogravimetric analysis of the spent catalysts were performed on a Mettler–Toledo TGA/DSC-1 synchronous thermal analyzer (Mettler, Toledo, Zurich, Switzerland). Each sample (20 mg) was heated in the range of 50 to 800 °C at 10 °C min^{−1} under oxygen flow, and the weight loss was recorded.

3.3. Catalytic Tests

The catalytic tests for butene oligomerization to liquid products were performed on a fixed-bed down-flow reactor (assembled by ourselves). The testing system comprises a tubular packed bed (Φ_{int} 10 mm, length 550 mm). Temperature was controlled by an electrical oven with three independent heating zones. In each test, about 2 g of catalyst was fed into the reactor. Typically, a feedstock containing n-butene (99.99%) was introduced into the reactor with a double-plunger pump at 473 K and 573 K, under 1.5 MPa and a WHSV (weight hourly space velocity) of 6 h^{−1}. The liquid products were injected into a gas chromatograph by a VICI pressure-lock precision analytical syringe (Baton Rouge, LA, USA). The liquid products were detected continuously by GC-FID (SP3420A) equipped with a PONA capillary column and identified by GC/MS analysis. The separated light hydrocarbons, cracking products (C₁~C₄) were analyzed using a gas chromatograph (SHIMADZU2010 plus, Tokyo, Japan) equipped with a GS-Alumina 50 m × 0.53 mm capillary column. The conversion was reported in terms of depleted butene fraction, and the C₈⁺ selectivity was reported as containing eight and more carbons atoms of the hydrocarbon components.

The butene conversion is defined in Equation (1):

$$C(\%) = \frac{n_{\text{int}} - n_{\text{out}}}{n_{\text{int}}} \times 100\% \quad (1)$$

where C is butenes conversion, n_{int} is amount of butenes in feed, n_{out} is amount of butenes in products.

The C₈⁺ selectivity to liquid fuels is defined in Equation (2):

$$S_{\text{C}_8^+}(\%) = \frac{\sum n_{x(x \geq 8)}}{\sum n_i} \times 100\% \quad (2)$$

$S_{\text{C}_8^+}$ is C₈⁺ selectivity, n_i is a selectivity for i -th component in products (contain the cracking side products such as light olefins), n_x is amount of x ($x \geq 8$) component in products.

4. Conclusions

We prepared a series of new types of hierarchical HZSM-5 zeolite catalysts (micro-mesoporous materials) by treating HZSM-5 with LiOH, NaOH, KOH, and CsOH aqueous solutions at the same concentration, respectively. The as-obtained materials were used as modified catalysts and tested for butene oligomerization. The results illustrated that the modified hierarchical HZSM-5 catalysts were more resistant to deactivation through pore blockage compared with the commercial ZSM-5 catalyst. Notably, the CsOH-treated hierarchical HZSM-5 catalyst not only showed suitable acidity and higher L/B ratio, but also presented interconnected open-mesopores and a smaller crystal size, resulting in higher catalytic activity and stability owing to the presence of shorter diffusion paths.

Furthermore, the ATHZ5-Cs catalyst with shorter diffusion paths and suitable acidity can better prolong the catalyst lifetime for butene oligomerization. Particularly, the ATHZ5-Cs catalyst was the most effective catalyst, resulting in approximately 92% conversion of butene and C_8^+ selectivity of 85% within 12 h. The ATHZ5-Cs catalyst can satisfy the oligomerization process and has the potential to be used as a substitute for the commercial ZSM-5 catalyst. Above all, it could be speculated that modifying the acidity properties and hierarchical structure of the zeolitic catalyst are crucial for enhancing the catalytic activity and stability in the oligomerization process.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/8/7/298/s1>, Figure S1: Major reaction mechanism for oligomerization of butene, Figure S2: Conversion and C_8^+ selectivity of catalytic oligomerization of HZ5 catalyst and modified catalysts. Reaction condition: temperature 473 K, pressure 1.5 MPa, time 2 h.

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