



Article Facile Synthesis of Nanosheet-Stacked Hierarchical ZSM-5 Zeolite for Efficient Catalytic Cracking of n-Octane to Produce Light Olefins

Peng Wang ¹, Xia Xiao ^{1,*}, Yutong Pan ¹, Zhen Zhao ^{1,2,*}, Guiyuan Jiang ^{2,*}, Zhongdong Zhang ^{3,*}, Fanfang Meng ³, Yuming Li ², Xiaoqiang Fan ¹, Lian Kong ¹ and Zean Xie ¹

- ¹ Institute of Catalysis for Energy and Environment, Shenyang Normal University, Shenyang 110034, China; pengw0511@163.com (P.W.); yutongpan2022@126.com (Y.P.); fanxiaoqiang@synu.edu.cn (X.F.); konglian@synu.edu.cn (L.K.); xiezean@synu.edu.cn (Z.X.)
- ² State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China; liyuming@cup.edu.cn
- ³ Petrochemical Research Institute, PetroChina, Beijing 102206, China; mengfanfang@petrochina.com.cn
- * Correspondence: xiaoxia@synu.edu.cn (X.X.); zhenzhao@cup.edu.cn (Z.Z.); jianggy@cup.edu.cn (G.J.); zhangzhongdong@petrochina.com.cn (Z.Z.); Tel.: +86-24-86579800 (Zhen Zhao)

Abstract: The development of an effective strategy for synthesizing two-dimensional MFI zeolites has attracted more and more attention. Herein, nanosheet-stacked hierarchical ZSM-5 zeolite was obtained by a seed-assisted hydrothermal synthesis route using a small amount of $[C_{18}H_{37}-N^+(CH_3)_2-C_6H_{12}]Br_2$ ($C_{18-6-6}Br_2$) as a zeolite structure-directing agent and triethylamine (TEA) as a zeolite growth modifier. By varying the molar ratio of $C_{18-6-6}Br_2$ /TEA from 2.5/0 to 2.5/40, the morphologies and textural properties of the resultant HZ5-2.5/x catalysts were finely modulated. By increasing x from 5 to 40, the morphology of the HZ5-2.5/x changed from unilamellar assembly with narrow *a*-*c* plane to intertwined nanosheets with wide *a*-*c* plane and multilamellar nanosheets with house-of-cards morphology. The thickness of these nanosheets was almost 8–10 nm. In addition, selectivity to light olefins reached 70.7% for the HZ5-2.5/10 catalyst, which was 6.6% higher than that for CZSM-5 (64.1%). Furthermore, the MFI zeolite nanosheets exhibited better anticoking stability within the 60 h reaction time compared to conventional ZSM-5 zeolite, which could be attributed to the short diffusion path and hierarchical porosity. This work will provide valuable insights into the rational design of novel zeolite catalysts for the efficient cracking of hydrocarbons.

Keywords: ZSM-5; nanosheets; zeolite growth modifiers; catalytic cracking of n-octane; light olefins

1. Introduction

Light olefins, such as ethylene, propylene, and butylene, are important building blocks for the production of various polymers and other value-added chemicals [1,2]. Over the past half-century, traditional tubular steam cracking of hydrocarbons has been the main technology for the production of light olefins [3]. However, the steam cracking process has some disadvantages, such as high reaction temperature (higher than 800 °C), high amount of CO₂ emission, low yield of propylene, and strict limit for the types of feedstock [4]. With the challenges of energy shortage and increasingly strict environmental protections, catalytic cracking of hydrocarbons over zeolites to produce light olefins has been considered as a promising alternative and has attracted widespread attention in the petrochemical industry [5,6].

Zeolites are crystalline aluminosilicate materials that have been widely used as catalysts in the petrochemical industry because of their tunable acidity, large surface area, unique shape selectivity, high thermal stability, and uniform micropores [7,8]. HZSM-5 zeolites are currently considered as one of the most ideal cracking catalysts [9,10]. However, the



Citation: Wang, P.; Xiao, X.; Pan, Y.; Zhao, Z.; Jiang, G.; Zhang, Z.; Meng, F.; Li, Y.; Fan, X.; Kong, L.; et al. Facile Synthesis of Nanosheet-Stacked Hierarchical ZSM-5 Zeolite for Efficient Catalytic Cracking of n-Octane to Produce Light Olefins. *Catalysts* **2022**, *12*, 351. https:// doi.org/10.3390/catal12030351

Academic Editors: Qinghua Lai, Qingfeng Zhang and Run-Ping Ye

Received: 12 February 2022 Accepted: 17 March 2022 Published: 21 March 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). single microporosity means MFI zeolites suffer from intracrystalline diffusion limitations. This leads to some active sites being hindered from contact with bulky molecules. Coke deposition in the microporous channels can cause rapid deactivation of MFI zeolite catalysts. Thus, the activity, selectivity to light olefins, and even the lifetime of the catalysts in catalytic cracking reaction are affected [11–13]. Many efforts have been made to alleviate the diffusional limitations by introducing additional intracrystalline meso/macropores [14,15] or inhibiting zeolite crystal growth beyond the nanometer scale [16]. Another efficient strategy for enhancing diffusion in microporous zeolites is to reduce the length of the diffusion path in the crystal by decreasing the thickness of zeolite crystals (or framework) [17,18].

In recent years, there has been a great deal of interest in two-dimensional zeolites due to their remarkable catalytic performance in a variety of reactions [19,20] and excellent separation ability in membrane applications [21]. Notably, Ryoo's group designed the bifunctional diquaternary ammonium-type surfactant $[C_{22}H_{45}N(CH_3)_2C_6H_{12}N(CH_3)_2C_6H_{13}]Br_2$ as a structure-directing agent (SDA) to successfully prepare an MFI zeolite with nanosheet-like morphology and thickness of 2 nm along the *b*-axis [18]. As reduction in crystal thickness greatly facilitates diffusion and therefore dramatically suppresses catalyst deactivation through coke deposition, the MFI nanosheets exhibited a tremendously long catalytic lifetime in methanol-to-hydrocarbon catalytic conversion [18] and hydrocarbon catalytic cracking reaction [22,23]. Our previous work also demonstrated that ZSM-5 nanosheets with macro-/meso-/microporosity and highly exposed (010) crystal planes showed high activity and good anticoking stability in the catalytic cracking of n-heptane [24]. Moreover, a large number of accessible acid sites on the external surface of these zeolite nanosheets make them suitable for the catalytic conversion of large organic molecules [25]. However, it is worth noting that MFI zeolite nanosheets are synthesized using the complex and expensive organic diquaternary ammonium surfactant as SDA, which not only increases the cost of zeolites but also produces harmful gases by calcination at high temperature to remove organic templates. Therefore, the utilization of low-cost organic additives to realize effective synthesis of MFI zeolite nanosheets has important research significance.

Previous studies have demonstrated that zeolite crystal engineering is one of the most effective methods to modulate the morphology of zeolites [26,27]. Rimer and coworkers reported that the introduction of zeolite crystal growth modifiers (ZGMs), a special type of additive in the zeolite synthetic system, can control the morphology of L zeolite crystals [28]. Furthermore, Rimer's group successfully applied this approach to tailor the crystal size and morphology of silicalite-1 [29,30] and SSZ-13 [31] zeolites. Zhang et al. reported that nanosized zeolite single crystals or hierarchical ZSM-5 nanocrystals could be generated using L-lysine as a crystal growth modifier through kinetic-modulated crystallization [32]. Song et al. developed an effective strategy to regulate the morphologies and the Ti coordination states of TS-1 zeolites using the amino acid L-carnitine as a crystal growth modifier and ethanol as a cosolvent [33]. Growth modifier molecules can interact with specific crystal surface zeolites or associate with amorphous precursors to tailor the anisotropic growth rates of zeolite crystals, thus generating zeolite crystals with well-defined size and shape.

Therefore, the fabrication of MFI zeolites with desirable morphologies, short diffusion pathway, tunable acid properties, and thus enhanced catalytic performances is a pervasive challenge in zeolite crystal engineering. Here, we report the synthesis of hierarchical ZSM-5 zeolite nanosheets with controlled crystal properties (i.e., morphology, acidity, and mesoporosity) by integrated a small amount of the Gemini quaternary ammonium surfactant $C_{18}H_{37}$ -N⁺(CH₃)₂-C₆H₁₂-N⁺(CH₃)₂-C₆H₁₂]Br₂ (C₁₈₋₆₋₆Br₂) as a structure-directing agent (SDA) and triethylamine (TEA) as a zeolite growth modifier (ZGM). The influence of the molar ratio of $C_{18-6-6}Br_2/TEA$ on the resultant HZ5-2.5/x catalysts was investigated. Our results indicate that the crystal engineering strategy is a facile method for cooperative tuning of the crystal properties of MFI zeolite nanosheets that are critical to their catalytic performance, such as textural properties, morphology, and acid properties, by tuning the concentration of triethylamine growth modifiers. The benefits of hierarchical porosity and more accessible acid sites mean HZ5-2.5/10 catalysts are able to exhibit superior catalytic ac-

tivity and excellent stability in the catalytic cracking of n-octane compared to conventional ZSM-5 zeolites.

2. Results and Discussion

2.1. The Crystalline Structure of the ZSM-5 Catalysts

Figure 1 shows the wide-angle X-ray diffraction (XRD) patterns of the ZSM-5 zeolite catalysts. As shown in Figure 1a, all the samples showed a typical MFI structure from the standard PDF card (JCPDS-44-0003) [34,35]. The diffraction peaks at 7.9, 8.9, 23.2, and 24.0° were assigned to the (101), (200), (501), and (303) planes of the MFI framework, respectively. No other crystalline phases or amorphous silica phases were detected, indicating that the resultant products were pure ZSM-5 crystals with high crystallinity. The HZ5-0/0 was simply a conventional microporous MFI zeolite. As shown in Figure 1b, the resulting HZ5-2.5/x samples showed broader diffraction peaks with weaker intensity than those observed for the conventional ZSM-5 sample. This XRD diffraction peak broadening phenomenon for HZ5-2.5/x samples was consistent with previously reported observations on the synthesis of nanosized ZSM-5 [36] or hierarchical ZSM-5 [37]. It is worth noting that most of the representative diffraction peaks of the HZ5-2.5/x samples corresponded to the h0l reflections of the MFI structure, indicating that MFI nanosheets preferentially grew along the a-c planes and that the thickness of the crystals along b-axis was extremely small [38,39]. The XRD results indicate that TEA plays an important role as a kind of zeolite growth modifier in the formation of sheet-like ZSM-5 crystals.



Figure 1. XRD patterns of the ZSM-5 zelite samples were detected in the range of $5-50^{\circ}$ (**a**) and 22.5-25° (**b**), respectively.

The Fourier transform infrared (FTIR) spectra of the as-prepared ZSM-5 samples and the conventional ZSM-5 are shown in Figure 2. Figure 2a shows the IR spectra of the ZSM-5 catalysts detected in the range of 2000–400 cm⁻¹. All the samples presented the characteristic IR vibrational bands at about 540 cm⁻¹, which were attributed to the asymmetric stretching of the five-membered ring of Si–O–Si or Si–O–Al for the ZSM-5 type zeolite [34]. The IR vibrational bands at 445, 795, 1080, and 1220 cm⁻¹ were due to the T–O bend, external symmetric stretching, internal asymmetric stretching, and external asymmetric stretching, respectively, originating from HZSM-5 [34]. As can be seen from Figure 2b, weak IR bands at ca. 3730 and 3600 cm⁻¹ were attributed to the vibration of OH from Si(OH) and the vibration of bridged OH in Si(OH)Al [34]. These results indicated that the amount of triethylamine addition had little effect on the ZSM-5 framework structure.



Figure 2. FTIR spectra of the ZSM-5 samples were detected in the range of $2000-400 \text{ cm}^{-1}$ (**a**) and $4000-3500 \text{ cm}^{-1}$ (**b**), respectively.

2.2. The Morphology of the ZSM-5 Catalysts

Figure 3 displays the SEM and TEM images of the as-prepared ZSM-5 zeolite samples. When the $C_{18-6-6}Br_2$ surfactant was absent in the synthesis of zeolite, the obtained HZ5-0/0 sample showed hexagonal plate-like morphology with an average size of 1.0 μ m and a uniform thickness of about 150 nm (Figure 3A,a). However, HZ5-2.5/0 exhibited a nanocrystalline aggregate shape with a size of about 1.6 μ m, which was composed of elongated needle-like crystals (Figure 3B,b). Moreover, with the increase in the TEA amount, the morphology of the HZ5-2.5/x samples varied extensively. When x was increased from 0 to 5, a significant difference could be observed for the HZ5-2.5/5 sample, which was assembled into platelet-like crystals with a very narrow a-c plane and a short dimension along the *b*-axis (Figure 3C,c). The crystals of HZ5-2.5/5 had an average size of 1.2 μ m, and the nanosheets were about 8 nm thickness along the *b*-axis dimension of the MFI crystal lattice. The crystal morphology of the HZ5-2.5/10 sample was similar to that of the HZ5-2.5/5 sample with an unordered array in the form of two-dimensional lamellar MFI zeolite (Figure 3D). TEM image (Figure 3d) showed that each flower-like particle was composed of nanosheets with a thickness of 10 nm. When the x value further increased from 10 to 20, the intergrowth leaf-like morphology with well-developed *a*–*c* plane and a short dimension along the *b*-axis was observed for the HZ5-2.5/20 sample (Figure 3E). As shown in Figure 3e, these leaf-like particles of $1.5 \ \mu m$ were composed of nanosheets with a thickness of 8 nm. The ZSM-5 nanosheets were oriented along the perpendicular directions and intersected one another to form a hierarchical structure [40,41]. When the x value reaches 40, as shown in Figure 3F, the resulting HZ5-2.5/40 sample exhibited intertwined nanosheet-like particles, similar to the multilamellar MFI reported by Na et al. [18]. The crystals of HZ5-2.5/40 had an average size of 2.0 μm. In fact, the observed thick layers were composed of multilayer nanosheet stacks, and the thickness of *b*-axis was also about 8 nm (Figure 3f). Interestingly, this intergrowth manner of ultrathin ZSM-5 plates was similar to the case of repeated branching plates that propagated into a house-ofcards morphology [42], and the hierarchical morphology resembled self-pillared pentasil (SPP) zeolites [43]. These results demonstrated that the thickness of ZSM-5 crystals (along the *b*-axis) was significantly reduced to about 10 nm after adding a certain amount of $C_{18-6-6}Br_2$ surfactant and triethylamine to the sol–gel system. Therefore, we speculated that there may be a synergetic effect between $C_{18-6-6}Br_2$ and TEA growth modifiers. The morphology information from the SEM and TEM images was in good agreement with the XRD patterns. Moreover, the amount of TEA zeolite growth modifiers played an important role in adjusting the morphology of the ZSM-5 zeolite. This may be because TEA molecules have specificity for binding crystallographic surfaces and can thus regulate the anisotropic growth of ZSM-5 crystals.



Figure 3. SEM and TEM images of the ZSM-5 zeolite samples. (**A**,**a**) HZ5-0/0, (**B**,**b**) HZ5-2.5/0, (**C**,**c**) HZ5-2.5/5, (**D**,**d**) HZ5-2.5/10, (**E**,**e**) HZ5-2.5/20, and (**F**,**f**) HZ5-2.5/40.

2.3. The Textural Properties of the ZSM-5 Catalysts

The textural properties of the ZSM-5 samples were further analyzed by nitrogen physisorption. The nitrogen adsorption-desorption isotherms and pore size distribution of these samples are shown in Figure 4a, b, respectively. From Figure 4a, it can be seen that the as-synthesized HZ5-0/0 showed characteristic I-type isotherms, indicating that only micropores existed in the ZSM-5 zeolite. The introduction of mesoporosity upon additional $C_{18-6-6}Br_2$ surfactant was clearly revealed by the N₂ adsorption–desorption isotherms from the transformation of the type I isotherm into type I and type IV isotherms of the HZ5-2.5/x samples, indicating that both micropores and mesopores existed in the as-synthesized ZSM-5 zeolite [44]. The adsorption phenomenon may be related to the hysteresis loop of the samples. Because the hysteresis loop had the general form of H_3 type, the nanosheets may accumulate to form slit pores [45,46]. Correspondingly, the Barrett–Joyner–Halenda (BJH) model was used to estimate the mesoporous size distributions of the samples. As shown in Figure 4b, the BJH curves of the HZ5-0/0 and CZSM-5 indicated that the two samples contained only micropores. However, the HZ5-2.5/x samples showed a broad mesoporous distribution in the range of 10–50 nm, indicating that the in situ assembly of these nanosheet crystallites gave rise to abundant intercrystal mesopores within these zeolite particles [47].



Figure 4. N₂ adsorption–desorption isotherms (**a**) and the corresponding BJH pore size distribution of the as-prepared ZSM-5 samples (**b**).

The pore structural properties of the ZSM-5 samples analyzed from N2 adsorptiondesorption isotherms are summarized in Table 1. As can be seen, the BET surface area (S_{BET}) of HZ5-0/0 was the smallest at only 275 m²/g. The micropore volume (V_{micro}) of the obtained HZ5-2.5/x samples was similar to CZSM-5. However, the S_{BET} and total pore volumes (V_{tol}) of the obtained HZ5-2.5/x samples was larger than that of CZSM-5. Specifically, the external surface area (S_{ext}) of the HZ5-2.5/20 sample reached 261 m²/g, which was almost 3 times that of CZSM-5 (94 m^2/g). Moreover, the enhanced S_{ext} was mainly attributed to the decrease in crystal size of the ZSM-5 zeolite. Interestingly, we observed that the V_{tol} of the obtained HZ5-2.5/10 sample reached 0.42 cm³/g, which was 2 times that of the micropores of CZSM-5 ($0.20 \text{ cm}^3/\text{g}$). These results demonstrate that the introduction of triethylamine could regulate the textural properties of ZSM-5 zeolites. The concept of hierarchy factor (hereafter referred to as HF) was first proposed by Pérez-Ramírez and coworkers to comprehensively describe the contribution of the pore structure to the catalytic effect [48]. Hao et al. proposed a derivation of HF (HF') to establish the relationship between the hierarchical pores of ZSM-5 nanosheets and its catalytic performance in the n-heptane cracking reaction [22]. Therefore, the HF' is listed in Table 1 to comprehensively compare the effect of mesopores and micropores on catalytic properties. When the x increased from 0 to 10, the HF' increased from 1.16 to 1.73. A further increase of x from 10 to 40 resulted in HF' decreasing from 1.73 to 1.21 (Table 1). Generally speaking, the variation of textural properties in mesoporous zeolitic materials are closely related to the assembling state of the surfactant micelle [49], crystal size, and shape of zeolite [50]. The variation of HF' value may be related to the different assembling methods of intergrown zeolite nanosheets. This result reveals that growth modification is a highly efficient and facile method for preparing zeolites with tailored mesoporous properties.

Table 1. Si/Al ratio and textural properties of the as-prepared ZSM-5 samples.

Samples	Si/Al ¹	$S_{BET}(m^2/g)^2$	$S_{ext}(m^2/g)^3$	V_{tol} (cm ³ /g) ⁴	V _{micro} (cm ³ /g) ⁵	HF′ ⁶
HZ5-0/0	-	275	128	0.11	0.08	0.19
HZ5-2.5/0	55	421	222	0.32	0.10	1.16
HZ5-2.5/5	57	416	222	0.42	0.10	1.71
HZ5-2.5/10	59	412	219	0.42	0.10	1.73
HZ5-2.5/20	56	447	261	0.38	0.10	1.68
HZ5-2.5/40	57	432	208	0.41	0.12	1.21
CZSM-5	48	320	94	0.20	0.10	0.29

¹ Si/Al was determined by XRF; ² S_{BET} was determined by BET equation; ³ S_{ext} is the external specific surface area calculated by the *t*-plot method; ⁴ V_{tol} was calculated by the BJH method; ⁵ V_{micro} was calculated by the *t*-plot method; ⁶ HF' = (V_{Meso}/V_{Micro}) × (S_{ext}/S_{BET}).

2.4. The Formation Mechanism of Hierarchical ZSM-5 Nanosheets

The proposed formation mechanism of layered ZSM-5 zeolite is described by schematic illustrations in Figure 5. With hydrolysis of the initial synthesis gel, hydrophilic moieties, such as AlO_x^- , SiO_x^- , H_2O , and $C_{18-6-6}Br_2$ surfactant micelles, were formed. In the early stage of crystallization, soluble silicon/aluminum monomers or oligomers agglomerated into small amorphous nanoparticles [51]. During the high temperature crystallization process, the MFI nanocrystals gradually grew under the direction of seeds and the $C_{18-6-6}Br_2$ structure-directing agents. Meanwhile, the hydrophobic tails of the $C_{18-6-6}Br_2$ surfactant inhibited growth of the zeolite crystals [18] and induced these nanoparticles to aggregate and form zeolite nanoneedles. Interestingly, it was found that at a low triethylamine growth modifier concentration, the obtained MFI layer had a narrow a-c plane and was randomly assembled to form a unilamellar structure. However, at high triethylamine growth modifier concentration, the MFI nanosheets were intertwined with a wide a-cplane. The results show that introduction of TEA can not only establish coordination with the monomer Si and Al species and the amorphous nanoparticles but also be used as an adsorbent to cover the preferential face of the crystal (i.e., the a-c plane) [33]. Under the present synthesis conditions, the MFI crystal growth in the a-c plane was favorable, which ultimately led to the formation of plate-like MFI zeolite crystals. With further increase in TEA concentration, these nanosheets were regularly stacked along the *b*-axis to form multilamellar assembly. The intergrowths of the zeolite nanosheets were enhanced during the crystal growth process. Subsequently, the intertwined multilamellar evolved into the house-of-cards MFI zeolite nanosheet assembly with a hierarchical structure.



Figure 5. Graphic illustration of the formation of hierarchical ZSM-5 nanosheets in hydrothermal crystallization with different amounts of triethylamine addition.

2.5. The Acid Properties of ZSM-5 Catalysts

It is well known that the amount, strength, and type of acid sites in ZSM-5 zeolites play an important role in the catalytic cracking of hydrocarbons [52,53]. Therefore, NH₃-TPD measurements were performed to evaluate the effect of TEA addition on the acidity of ZSM-5 catalysts [54]. As can be seen from the NH₃-TPD profiles in Figure 6, two distinct NH₃ desorption peaks of these zeolite samples appeared at 160 and 380 °C, which was assigned to the desorption of NH₃ from weak and strong acid sites, respectively [55]. As shown in Figure 6, the temperature of NH₃ desorption from the strong acid sites was higher in the HZ5-2.5/5 sample (ca. 380 °C) than in the HZ5-2.5/0 sample (ca. 355 °C), indicating stronger acid strength of the HZ5-2.5/5 sample compared to the HZ5-2.5/0 sample. Meanwhile, on the basis of the desorption peak areas of NH₃, the strong acid content of HZ5-2.5/5 was evidently increased compared to HZ5-2.5/0. Comparing the acid properties of HZ5-2.5/x in Figure 6, we observed that the HZ5-2.5/5, HZ5-2.5/10, and HZ5-2.5/20 samples had similar NH₃-TPD profiles, illustrating that the total acid content and acid strength were roughly the same. All the as-prepared ZSM-5 samples had comparable Si/Al molar ratio between 55 and 59 according to the XRF analysis (Table 1). This result was consistent with the comparable Si/Al molar ratio as indicated by XRF. The acidity of the above three samples were similar to that of CZSM-5. In addition, it was found that the intensity of the NH₃ desorption peak around 380 °C decreased slightly as the x increased from 20 to 40, indicating that the number of strong acid sites in the HZ5-2.5/40 catalyst was less than those in the HZ5-2.5/20 catalyst. This result demonstrates that the acidity of ZSM-5 zeolites can be tuned by introducing an appropriate amount of TEA.



Figure 6. NH₃-TPD profiles of the as-prepared ZSM-5 samples.

The type and concentration of acid sites was further investigated by Py-IR tests. Figure 7 shows the FTIR spectra of adsorbed pyridine for ZSM-5 catalysts after evacuation at 200 and 350 °C. The band at 1540 cm⁻¹ was the result of PyH⁺ created by protonation on Brønsted (B) acid sites, whereas the adsorption band around 1450 cm^{-1} was assigned to the coordinatively bounded pyridine on Lewis (L) acid sites in the zeolite catalysts [56]. In addition, the IR band at 1490 $\rm cm^{-1}$ was associated to the vibration of the pyridinic ring on B and L acid sites [56]. As shown in Figure 6, 1540 and 1450 cm⁻¹ bands appeared on the spectra of all the measured zeolite samples, indicating the coexistence of Brønsted and Lewis acid sites in the catalysts. Brønsted acid originates from the bridging hydroxyl group connected to tetracoordinated aluminum, while tricoordinated defect aluminum forms Lewis acid [57]. The concentrations of individual B and L acid sites of the ZSM-5 samples are shown in Table 2. Generally speaking, Brønsted acid sites have a profound influence on the catalytic activity during the hydrocarbon catalytic cracking reaction, thereby affecting product distribution [58,59]. As shown in Table 2, the concentration of total and strong Brønsted acid sites of the resultant HZ5-2.5/x samples first increased slightly with the introduction of small amounts of TEA and then decreased with further increase in the amount of TEA. Among them, the HZ5-2.5/20 sample exhibited the highest total Brønsted acid concentration (206.3 μ mol/g) and strong Brønsted acid concentration (102.7 μ mol/g). The density of the B acid sites decreased after the introduction of large amounts of TEA, which was in good agreement with the NH₃-TPD results. Moreover, it could be clearly seen that the density of total L acid sites also gradually increased with the increase in TEA content, reached a maximum value of 24.5 μ mol/g in HZ5-2.5/10, and then decreased with further increase in the amounts of TEA. At the same time, the Brønsted-to-Lewis acid site ratios $(_{CB}/_{CL})$ of the zeolite catalysts also changed. This result demonstrated that the modulation in textural properties and morphologies of the HZ5-2.5/x samples also affected their acidity.



Figure 7. FTIR spectra of adsorbed pyridine for the ZSM-5 samples after being degassed at 200 and 350 °C.

Table 2. Py-IR characterization results of the as-prepared ZSM-5 samples.

Samples	Concentration of B Acid Sites (µmol/g)			Concentration of L Acid Sites (µmol/g)			
	Weak and Med. (200 °C)	Strong (350 $^{\circ}$ C)	Total	Weak and Med. (200 °C)	Strong (350 $^{\circ}$ C)	Total	CB/CL
HZ5-2.5/0	82.3	75.9	158.2	6.4	4.6	11.0	14.4
HZ5-2.5/5	81.4	80.7	162.1	9.5	6.3	15.8	10.2
HZ5-2.5/10	84.6	78.6	163.2	16.9	7.6	24.5	6.7
HZ5-2.5/20	103.6	102.7	206.3	13.9	9.9	23.8	8.7
HZ5-2.5/40	62.0	54.3	116.3	6.2	4.8	11.0	10.6
CZSM-5	105.0	99.3	204.3	8.6	4.4	13.0	15.7

The ²⁷Al MAS NMR technique is a well-established tool to determine the coordination state of the aluminum species present in the zeolite sample. Figure 8 presents the ²⁷Al MAS NMR spectra of the HZ5-2.5/x samples. All the samples exhibited a main resonance signal located at 54 ppm, which corresponded to tetrahedrally coordinated framework aluminum atoms with Brønsted acid site [60]. However, the resonance of octahedral Al (0 ppm), which relates to octahedrally coordinated extra framework Al species (EFAl), was almost absent [60]. On the basis of the ²⁷Al MAS NMR results, we concluded that most of the aluminum species were tetrahedrally coordinated, with the Brønsted acid site mainly being responsible for the catalytic activity in cracking reactions. Therefore, the number of extra framework aluminum species with Lewis acid site was very small.

To investigate the different aluminum species in the as-prepared HZ5-2.5/x samples, the broad peak corresponding to tetrahedrally coordinated framework aluminum species was further deconvoluted into four peaks at around 49, 53, 56, and 58 ppm [60]. They were designated as Al(49), Al(53), Al(56), and Al(58), respectively (Figure S1), and the proportions of these peaks are listed in Table S1. The resonance peaks at 49, 53, and 58 ppm were related to the Al atoms located at T1 + T2 + T3, T5 + T6 + T7, T9, and T12 sites at the channel intersections, respectively [60]. The resonance peaks at 56 ppm correspond to Al atoms positioned at T4, T10, T8, and T11 sites in the straight 10-MR channels [60]. As can be seen from the results in Table S1, there were slightly differences in the proportion of as-prepared HZ5-2.5/x samples. The proportion of Al(56) roughly increased, while the proportion of Al(53) decreased with increasing TEA content. These results showed that the addition of an appropriate amount of TEA led to an increase in aluminum species located in the straight channels.



Figure 8. ²⁷Al NMR spectra of the as-prepared ZSM-5 samples.

3. Catalytic Cracking of n-Octane over the As-Prepared ZSM-5 Catalysts

In the present work, the cracking of n-octane, a typical probe reaction for the cracking of naphtha, was chosen to investigate the catalytic activity and product distribution of as-synthesized hierarchical ZSM-5 zeolites. Figure 9 shows the conversion of n-octane in the catalytic cracking reaction over the ZSM-5 catalysts. As can be seen from Figure 8, the conversion for all the ZSM-5 zeolite catalysts increased gradually as the reaction temperature increased from 500 to 650 °C. Compared to conventional ZSM-5 zeolite, the as-prepared HZ5-2.5/x catalysts exhibited a higher conversion of n-octane. The results showed that the as-prepared HZ5-2.5/x catalysts had higher catalytic activity compared to CZSM-5. The conversion of n-octane for HZ5-2.5/40 at 500 °C reached 81.1%, which was 19.1% higher than that of CZSM-5, indicating that the catalytic activity was significantly improved. It is generally accepted that the amount of Brønsted acid sites of ZSM-5 catalysts plays an important role in cracking activity [61,62]. Although the concentration of Brønsted acid sites in HZ5-2.5/40 sample was much lower than that of CZSM-5, the former showed higher catalytic activity. Therefore, we think that the high activity of HZ5-2.5/40 sample may be attributed to the hierarchical zeolite nanosheets being exposed to more accessible acid sites. Similar results were reported in the literature [22,23].

Figure 10 shows the yield of light olefins in the catalytic cracking of n-octane over ZSM-5 catalysts. From Figure 9, it can be seen that the yield of light olefins over CZSM-5 showed a volcanic-like curve. It first increased with increasing temperature to a maximum of 66.2% at 600 °C and then decreased with further increase in temperature, which indicates that light olefin production is a very complicated reaction process. Previous studies have shown that the operating conditions of cracking reaction and the physicochemical properties of zeolite catalysts (acid properties, pore structure, crystal sizes) have a significant effect on light olefin production. Because light olefins are easily converted into by-products by hydrogen transfer and aromatization reactions, the yield of light olefins decreases noticeably [63]. However, the HZ5-2.5/x catalysts showed a different trend. Except for HZ5-2.5/40, the yield of light olefins for the HZ5-2.5/x catalysts increased gradually along with increasing reaction temperature. When the reaction temperature was 650 °C, HZ5-2.5/10 showed the highest light olefin yield of 70.5%, which was 6.7% higher than that of CZSM-5 (63.8%) under the same reaction conditions. Meanwhile, the yield of light olefins over HZ5-2.5/x at 650 °C first increased with increasing x value to a maximum of 10 and then decreased with further increase in x value. Among the as-prepared catalysts, the light olefin yield over HZ5-2.5/10 catalyst was the highest, mainly because of the higher hierarchy factor. The results showed that the hierarchy factor of ZSM-5 catalysts played an important role in obtaining high yield of light olefins during n-octane catalytic cracking.



Figure 9. Conversion of n-octane cracking over different ZSM-5 catalysts.



Figure 10. Yield of light olefins $(C_2^{=} + C_3^{=} + C_4^{=})$ over different ZSM-5 catalysts.

The selectivity to light olefins over the as-prepared HZ5-2.5/x catalysts at 650 °C is displayed in Figure 11, with the values for CZSM-5 also included as reference. As shown in Figure 11, the maximum selectivity to light olefins reached 70.7% over the HZ5-2.5/10 catalyst, which was 6.6% higher than that for CZSM-5 (64.1%) under the same reaction conditions. Compared to the CZSM-5 catalyst, HZ5-2.5/10 with ultrathin plates could significantly shorten the path length of the microporous channel, resulting in shorter residence time of light olefin molecules in the channel and thus achieving higher light olefin selectivity. As can be seen from the reaction results in Figure 11, the selectivity of light olefins over HZ5-2.5/x catalysts also showed a volcanic-like curve, first increasing with increasing x value and then decreasing with further increase in x value. Interestingly, we observed that the changing trend of light olefin selectivity was consistent with that of the HF' value of HZ5-2.5/x catalysts (Table 1). Considering that the average crystal *b*-axis thickness for HZ5-2.5/5, HZ5-2.5/10, HZ5-2.5/20, and HZ5-2.5/40 was similar (~8 nm), plates thickness was not taken as a factor affecting the selectivity of light olefins in this work. In addition, the selectivity of light olefins had little correlation with the acidity of the catalyst. Therefore, the possible reason for the higher light olefin selectivity for the HZ5-2.5/10 catalyst could be explained by the presence of a proper mesopores, which suppressed the secondary side reactions and consequently improved selectivity to light olefins.



Figure 11. Selectivity of light olefins ($C_2^{=} + C_3^{=} + C_4^{=}$) over different ZSM-5 catalysts. Reaction conditions: 0.5 g catalyst, WHSV = 2.8 h⁻¹, 650 °C.

ZSM-5 zeolites are active for hydrocarbon cracking into light olefins, but they have the disadvantage of fast deactivation. Therefore, a ZSM-5 with long lifetime, high activity, and anticoking stability has become the focus of industrial application. The prepared HZ5-2.5/10 and HZ5-2.5/40 catalysts were used to test stability, with CZSM-5 also included as reference. Changes in the conversion and yield of light olefins were examined along with the time on stream, and the stability evaluation results are shown in Figure 12. From Figure 12a, it can be seen that the n-octane conversion for both HZ5-2.5/10 and HZ5-2.5/40 catalysts was maintained at >96% during the 60 h reaction time, while n-octane conversion for CZSM-5 dropped sharply from 94.1 to 52.8%, with a reduction of 41.3% after 60 h on stream, suggesting that hierarchical HZ5-2.5/10 and HZ5-2.5/40 possessed higher initial activity and better stability than CZSM-5. As shown in Figure 12b, the light olefins yields of the HZ5-2.5/10 and HZ5-2.5/40 samples were maintained at >66 and >64%, respectively, during the 60 h reaction time, while the light olefin yield of CZSM-5 dropped rapidly from 62.6 to 38.5%, suggesting that the hierarchical zeolite had good anticoking stability, whereas CZSM-5 deactivated rapidly. Compared with CZSM-5, the enhanced catalytic stability of HZ5-2.5/10 and HZ5-2.5/40 could be attributed to the remarkably reduced diffusion lengths, which dramatically suppressed catalyst deactivation through coke deposition.

The coke contents of the spent HZ5-2.5/10, HZ5-2.5/40, and CZSM-5 catalysts were further determined by thermogravimetric analysis (Figure 13). Because the mass loss before 400 °C was due to the undesorbed products and the mass loss after 400 °C was attributed to coke, the coke contents of the spent HZ5-2.5/10, HZ5-2.5/40, and CZSM-5 catalysts were calculated according to the weight loss above 400 °C [35]. As shown in Figure 13, the coke content in the spent CZSM-5 catalyst was 10.3 wt%, which was 1.61-fold and 1.54-fold the content of the HZ5-2.5/10 (6.4 wt%) and HZ5-2.5/40 (6.7 wt%) catalysts, respectively. Therefore, the CZSM-5 catalyst exhibited poor catalytic stability. This was due to the diffusion resistance of the micropores, which resulted in much faster formation of coke than the hierarchical zeolites. The mesopores of the HZ5-2.5/10 and HZ5-2.5/40 catalysts were favorable for the diffusion of coke precursors out of the pores, which resulted in a reduction in coke content and thus improved stability.



Figure 12. The n-octane conversion (**a**) and yield of light olefins (**b**) with time on stream in the catalytic cracking of n-octane over different catalysts. Reaction conditions: 0.5 g catalyst, WHSV = 2.8 h^{-1} , $600 \degree$ C.



Figure 13. Thermogravimetric analysis results of the spent HZ5-2.5/10, HZ5-2.5/40, and CZSM-5 catalysts after 60 h reaction time.

4. Materials and Methods

4.1. Chemicals and Reagents

Tetraethyl orthosilicate (TEOS, >98%), triethylamine (TEA, >98%), aluminum isopropoxide (AIP, 98%), sodium hydroxide (NaOH, >96%), and ammonium chloride (NH₄Cl, 99%) were supplied by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. 1-Bromooctadecane (C₁₈H₃₇Br, 97%), 1-bromohexane (C₆H₁₃Br, 99%), and N,N,N,N,-tetramethyl-1,6-diaminohexane (C₁₀H₂₆N₂, 99%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China. Diethyl ether (C₄H₁₀O, 99%), toluene (C₇H₈, 98%), and acetonitrile (C₂H₃N, 99%) were purchased by Shanghai Chemical Co., Ltd., Shanghai, China. Deionized (DI) water was used throughout the experiment. The commercial ZSM-5 zeolite (CZSM-5) was provided by the catalyst plant of Nankai University, China. All chemicals and reagents were supplied by commercial suppliers and used without further purification.

4.2. Synthesis of Hierarchical Layered ZSM-5

A series of ZSM-5 zeolite samples were hydrothermally synthesized using the quaternary ammonium surfactant $[C_{18}H_{37}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{12}]Br_2$ (denoted as $C_{18-6-6}Br_2$) as the structure-directing agent (SDA), triethylamine (denoted as TEA) as the zeolite growth modifier (ZGM), and tetraethyl orthosilicate (TEOS) and aluminum isopropoxide (AIP) as the silicon and aluminum sources, respectively. The organic surfactant $C_{18-6-6}Br_2$ was synthesized based on the modified procedure in a previous report

by Ryoo and coworkers [18]. The impact of TEA on the formation of ZSM-5 zeolites was studied using the following molar composition: 7.5 Na₂O, 1 Al₂O₃, 125 SiO₂, 2.5 C₁₈₋₆₋₆Br₂, 4000 H₂O, and x TEA. The molar ratios of C₁₈₋₆₋₆Br₂/TEA were 2.5/0, 2.5/5, 2.5/10, 2.5/20, and 2.5/40, respectively. The as-obtained ZSM-5 zeolite samples were named after the C₁₈₋₆₋₆Br₂/TEA ratio as follows: HZ5-2.5/0, HZ5-2.5/5, HZ5-2.5/10, HZ5-2.5/20, and HZ5-2.5/40.

In a typical synthesis, 0.3 g of NaOH was dissolved in 6.0 mL of deionized water, followed by addition of 0.8376 g C₁₈₋₆₋₆Br₂ and stirring for 4 h at 40 °C to obtain the homogeneous solution A. Solution B was prepared by adding 0.2 g AIP, 13.0 g TEOS, and a certain amount of TEA in 30.0 mL deionized water and stirring for 4 h at 40 °C. Afterwards, solution A was slowly dropped into solution B and vigorously stirred for another 12 h at 60 °C. Then, 0.15 g ZSM-5 seeds was added to the above mixture and vigorously stirred for 0.5 h. The obtained suspension was transferred into a Teflon-lined autoclave, and crystallization of zeolites was conducted at 175 °C for 72 h. After that, the obtained sample was washed repeatedly with DI water and filtered. Then, it was successively dried at 100 °C for 12 h. To remove the organic contents, the obtained filter cakes were calcinated at 600 °C in air in a static muffle furnace for 6 h. To obtain the Htype ZSM-5 samples, ion exchange was processed three times in aqueous NH_4Cl solution (1 mol/L, m(liquid)/m(solid) = 30) under stirring at 80 °C for 4 h, followed by calcination at 600 °C in air for 4 h. For comparison, a conventional ZSM-5 sample was prepared by a similar procedure but without the addition of the diquaternary ammonium surfactant C₁₈₋₆₋₆Br₂ and the zeolite growth modifier TEA. The obtained product was referred to as HZ5-0/0.

4.3. Catalyst Characterization

X-ray diffraction (XRD) patterns were recorded with a RIGAKU Ultima IV (Tokyo, Japan) powder diffractometer equipped with a Cu K α (λ = 0.15406 nm) in the range of $5-50^{\circ}$ with a scan rate of 5° /min. Fourier transform infrared (FTIR) spectra were recorded on a Bruker VERTEX 80 (Billerica, MA, USA) in the range of 4000–400 cm^{-1} . The FTIR spectrometer was equipped with a mercury cadmium telluride (MCT) detector. A total of 64 scans were averaged for each spectrum. XRF (X-ray fluorescence) spectrum was recorded by a Thermo Scientific ARL ADVANT'X InliPower (Waltham, MA, USA) to determine the real percentage of Si and Al loading on the ZSM-5 zeolites. Scanning electron microscopy (SEM) images were recorded on a HITACHI FE-SEM SU8000 (Tokyo, Japan) instrument to visualize the morphologies of ZSM-5 zeolites. Transmission electron microscopy (TEM) pictures were taken on a FEI Talos F200X (Waltham, MA, USA) with an acceleration voltage of 200 kV. N₂ adsorption–desorption isotherms of the samples were measured at liquid nitrogen temperature (-196 °C) with a volumetric Micromeritics TriStarII 3020 (Atlanta, GA, USA) instrument. Prior to the adsorption measurement, all the samples were degassed at 90 °C under vacuum for 1 h, then heated up to 350 °C outgas for 4 h under 1×10^{-4} Pa. The specific surface area was calculated from the adsorption data obtained at P/P₀ between 0.05 and 0.20 using the Brunauer–Emmett–Teller (BET) equation. The total pore volume was derived from the nitrogen amount adsorbed at a relative pressure of 0.95. The external surface area and micropore volume were evaluated by the *t*-plot method. The mesopore volume and pore size distribution were evaluated by the Barrett-Joyner-Halenda (BJH) method on the adsorption branch of the isotherm. Temperature-programmed desorption of ammonia (NH₃-TPD) profiles were recorded with a Micromeritics AutoChem II 2920 (Atlanta, GA, USA) chemisorption apparatus. Samples (ca. 100 mg) were charged in a quartz tubular reactor and pretreated at 600 °C under He flow for 1 h and then cooled to 100 °C. NH₃ adsorption was carried out at 100 °C for 0.5 h. Then, He stream was fed in until a constant TCD signal was obtained, and the physisorbed ammonia was removed by flowing He at 100 °C for 1 h. The remaining chemically adsorbed ammonia was determined by increasing the temperature up to 600 $^{\circ}$ C with a heating rate of 10 $^{\circ}$ C/min, and the signal of desorbed NH₃ was simultaneously monitored by a thermal conductivity detector (TCD). Pyridine adsorption infrared spectra (Py-IR) were recorded on a Bruker Tensor 27 FTIR (Billerica, MA, USA) spectrometer. Prior to FTIR studies, the samples (ca. 10 mg) were pressed into a self-supported wafer in the absence of any binder and treated directly in an in situ IR cell at 450 °C under vacuum conditions for 2 h, which allowed residual pressure below 10⁻³ Pa to be obtained. Adsorption of pyridine proceeded at 25 °C, followed by desorption at 200 and 350 °C. The total concentration of the Brønsted acid sites (CB) and the Lewis acid sites (CL) in the samples was determined in quantitative IR studies of pyridine sorption according to the procedure described in a previous paper [34]. The solid-state ²⁷Al MAS NMR experiments were recorded on a Bruker Avance III 600M apparatus (Billerica, MA, USA). ²⁷Al MAS NMR spectra were collected at a resonance frequency of 130.32 MHz with a sample-spinning rate of 14 kHz, pulse-width of 1.0 µs, and recycling delay of 500 ms. Hydrated Al $(NO_3)_3$ powder was used as an external reference. Thermogravimetric analysis was performed on a NETZSCH-Gerätebau GmbH STA449F5 Jupiter TGA/DSC instrument (Selb, Germany) to determine the total amount of coke. The experiment was carried out with about 10 mg coked catalyst under an 80 mL/min air flow, and the ramp rate was $10 \,^{\circ}C/min.$

4.4. Catalytic Activity Measurement

Catalytic cracking of n-octane was used as a model reaction to test the catalysts. The n-octane cracking reaction was carried out in a continuous-flow fixed-bed tubular quartz reactor (10 mm i.d.) under atmospheric pressure. In a typical run, 500 mg of the catalyst sample was placed in the fixed-bed reactor and activated in flowing N₂ at 600 °C for 1 h prior to the reaction. Then, N₂ (100 mL/min) acting as the carrier gas delivered the n-octane into the catalyst bed. The reaction temperature and the weight hourly space velocity (WHSV) were 500–650 °C and 2.8 h⁻¹, respectively. The reaction products were analyzed online by an Agilent GC-7890B gas chromatograph equipped with an FID detector with an HP-PLOT/Al₂O₃ capillary column (50 m, 0.32 mm, 8 µm) and an HP-INOWax column (30 m, 0.32 mm, 0.5µm). The products were grouped into the following lumps: dry gas, such as CH₄ plus C₂H₆; light olefins, such as C₂H₄ and C₃H₆; paraffins, such as C₃H₈ and C₄H₁₀; BTX aromatics, including benzene, toluene, and xylenes; and C₅⁺ aliphatics (olefins and paraffins). The n-octane conversion (X), selectivity for products (S), and product yield (Y) were calculated by the following formulas:

$$X = \frac{m(C_8H_{18})_{in} - m(C_8H_{18})_{out}}{m(C_8H_{18})_{in}} \times 100\%$$
(1)

$$S = \frac{mC_xH_y}{\sum m(C_iH_j)} \times 100\%$$
⁽²⁾

$$Y = S \times X \tag{3}$$

where $m(C_8H_{18})_{in}$ and $m(C_8H_{18})_{out}$ are the mass fraction of n-octane before and after the reaction, $m(C_xH_y)$ is the mass fraction of products, and $\sum m(C_iH_j)$ is the sum of the mass fraction of products.

5. Conclusions

In summary, we developed a facile strategy to synthesize nanosheet-stacked hierarchical ZSM-5 zeolites. During the hydrothermal synthesis process, a small amount of the Gemini quaternary ammonium surfactant $[C_{18}H_{37}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{12}]Br_2$ $(C_{18-6-6}Br_2)$ was used as a zeolite structure-directing agent, while triethylamine (TEA) was used as a zeolite growth modifier. The former played an important role in the formation of MFI frameworks and mesopores, while the latter played a key role in the generation of two-dimensional zeolite nanosheets. In addition, we investigated the effects of the amount of TEA on the physicochemical properties of ZSM-5 zeolites. The results demonstrated that the morphology of the as-obtained HZ5-2.5/x sample changed from elongated needles to unilamellar nanosheets, intertwined nanosheets, and then house-of-cards nanosheets by tuning the molar ratio of $C_{18-6-6}Br_2/TEA$ from 2.5/0 to 2.5/40. The derivation of hierarchy factor (HF') increased to reach a maximum of 1.73 and then decreased with further increase in x value, indicating a systematic tailoring of the mesoporosity with TEA concentration. The varying Brønsted-to-Lewis acid site ratios suggested that the adjustment in textural properties and morphologies of the catalysts also affected their acidity. The HZ5-2.5/10 zeolite showed superior catalytic activity and stability for the catalytic cracking of n-octane, which could be attributed to the enriched accessible acid sites and hierarchical porosity caused by the unique nanosheet-like morphology. This synthesis strategy may bring new opportunities to develop more efficient nanoporous materials with improved performance for a range of important catalytic applications.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/catal12030351/s1, Figure S1: Deconvolution of the ²⁷Al MAS NMR spectra of the as-prepared ZSM-5 zeolites. The experimental spectra are in black line and the fitted spectra are shown in orange dashed line; Table S1: Distribution of Al species determined by deconvolution of the ²⁷Al MAS NMR spectra of the as-prepared ZSM-5 zeolites.

Author Contributions: Conceptualization, X.X.; data curation, Y.P.; formal analysis, P.W.; funding acquisition, Z.Z. (Zhen Zhao) and G.J.; investigation, P.W.; methodology, X.X.; project administration, Z.Z. (Zhen Zhao), G.J. and Z.Z. (Zhongdong Zhang); resources, Z.Z. (Zhongdong Zhang); software, Y.P.; supervision, Z.Z. (Zhen Zhao) and G.J.; validation, F.M. and Y.L.; visualization, Z.X.; writing—original draft, P.W.; writing—review and editing, X.X., Z.Z. (Zhen Zhao), X.F. and L.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Foundation of PetroChina Petrochemical Research Institute (Grant No. HX20210232), the National Natural Science Foundation of China (Grant No. 21802098, 91845201), and the Doctoral Research Initiation Project of Shenyang Normal University (Grant No. BS201801).

Data Availability Statement: The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Alabdullah, M.; Rodriguez-Gomez, A.; Shoinkhorova, T.; Dikhtiarenko, A.; Chowdhury, A.D.; Hita, I.; Kulkarni, S.R.; Vittenet, J.; Sarathy, S.M.; Castaño, P.; et al. One-step conversion of crude oil to light olefins using a multi-zone reactor. *Nat. Catal.* 2021, 4, 233–241. [CrossRef]
- 2. Palčić, A.; Catizzone, E. Application of nanosized zeolites in methanol conversion processes: A short review. *Curr. Opin. Green Sustain. Chem.* **2021**, 27, 100393. [CrossRef]
- 3. Sadrameli, S.M. Thermal/catalytic cracking of hydrocarbons for the production of olefins: A state-of-the-art review I: Thermal cracking review. *Fuel* **2015**, *140*, 102–115. [CrossRef]
- 4. Akah, A.; Williams, J.; Ghrami, M. An Overview of Light Olefins Production via Steam Enhanced Catalytic Cracking. *Catal. Surv. Asia* **2019**, *23*, 265–276. [CrossRef]
- 5. Rahimi, N.; Karimzadeh, R. Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: A review. *Appl. Catal. A Gen.* **2011**, 398, 1–17. [CrossRef]
- 6. Blay, V.; Louis, B.; Miravalles, R.; Yokoi, T.; Peccatiello, K.A.; Clough, M.; Yilmaz, B. Engineering Zeolites for Catalytic Cracking to Light Olefins. *ACS Catal.* 2017, 7, 6542–6566. [CrossRef]
- 7. Primo, A.; Garcia, H. Zeolites as catalysts in oil refining. Chem. Soc. Rev. 2014, 43, 7548–7561. [CrossRef]
- 8. Papanikolaou, G.; Lanzafame, P.; Giorgianni, G.; Abate, S.; Perathoner, S.; Centi, G. Highly selective bifunctional Ni zeo-type catalysts for hydroprocessing of methyl palmitate to green diesel. *Catal. Today* **2020**, 345, 14–21. [CrossRef]
- Blay, V.; Epelde, E.; Miravalles, R.; Perea, L.A. Converting olefins to propene: Ethene to propene and olefin cracking. *Catal. Rev.* 2018, 60, 278–335. [CrossRef]
- 10. Alipour, S.M. Recent advances in naphtha catalytic cracking by nano ZSM-5: A review. Chin. J. Catal. 2016, 37, 671-680. [CrossRef]
- Konno, H.; Tago, T.; Nakasaka, Y.; Ohnaka, R.; Nishimura, J.-I.; Masuda, T. Effectiveness of nano-scale ZSM-5 zeolite and its deactivation mechanism on catalytic cracking of representative hydrocarbons of naphtha. *Microporous Mesoporous Mater.* 2013, 175, 25–33. [CrossRef]
- 12. Mochizuki, H.; Yokoi, T.; Imai, H.; Watanabe, R.; Namba, S.; Kondo, J.N.; Tatsumi, T. Facile control of crystallite size of ZSM-5 catalyst for cracking of hexane. *Microporous Mesoporous Mater.* **2011**, 145, 165–171. [CrossRef]

- Sazama, P.; Sobalik, Z.; Dedecek, J.; Jakubec, I.; Parvulescu, V.; Bastl, Z.; Rathousky, J.; Jirglova, H. Enhancement of activity and selectivity in acid-catalyzed reactions by dealuminated hierarchical zeolites. *Angew. Chem. Int. Ed. Engl.* 2013, 52, 2038–2041. [CrossRef] [PubMed]
- 14. Han, L.; Wang, R.; Wang, P.; Zheng, A.; Guo, Y.; Chen, Y.; Jiang, Q.; Lin, W. Hierarchical hollow Al-rich nano ZSM-5 crystals for highly selective production of light olefins from naphthenes. *Catal. Sci. Technol.* **2021**, *11*, 6089–6095. [CrossRef]
- Abildstrøm, J.O.; Kegnæs, M.; Hytoft, G.; Mielby, J.; Kegnæs, S. Synthesis of mesoporous zeolite catalysts by in situ formation of carbon template over nickel nanoparticles. *Microporous Mesoporous Mater.* 2016, 225, 232–237. [CrossRef]
- Tago, T.; Konno, H.; Nakasaka, Y.; Masuda, T. Size-Controlled Synthesis of Nano-Zeolites and Their Application to Light Olefin Synthesis. *Catal. Surv. Asia* 2012, 16, 148–163. [CrossRef]
- 17. Dai, W.; Kouvatas, C.; Tai, W.; Wu, G.; Guan, N.; Li, L.; Valtchev, V. Platelike MFI Crystals with Controlled Crystal Faces Aspect Ratio. J. Am. Chem. Soc. 2021, 143, 1993–2004. [CrossRef]
- Choi, M.; Na, K.; Kim, J.; Sakamoto, Y.; Terasaki, O.; Ryoo, R. Stable single-unit-cell nanosheets of zeolite MFI as active and long-lived catalysts. *Nature* 2009, 461, 246–249. [CrossRef]
- 19. Roth, W.J.; Nachtigall, P.; Morris, R.E.; Cejka, J. Two-dimensional zeolites: Current status and perspectives. *Chem. Rev.* **2014**, *114*, 4807–4837. [CrossRef]
- 20. Xu, L.; Sun, J. Recent Advances in the Synthesis and Application of Two-Dimensional Zeolites. *Adv. Energy Mater.* **2016**, *6*, 1600441. [CrossRef]
- Kim, D.; Jeon, M.Y.; Stottrup, B.L.; Tsapatsis, M. para-Xylene Ultra-selective Zeolite MFI Membranes Fabricated from Nanosheet Monolayers at the Air-Water Interface. Angew. Chem. Int. Ed. Engl. 2018, 57, 480–485. [CrossRef] [PubMed]
- Hao, J.; Cheng, D.; Chen, F.; Zhan, X. n-Heptane catalytic cracking on ZSM-5 zeolite nanosheets: Effect of nanosheet thickness. *Microporous Mesoporous Mater.* 2021, 310, 110647. [CrossRef]
- Tian, Y.; Zhang, B.; Liang, H.; Hou, X.; Wang, L.; Zhang, X.; Liu, G. Synthesis and performance of pillared HZSM-5 nanosheet zeolites for n-decane catalytic cracking to produce light olefins. *Appl. Catal. A Gen.* 2019, 572, 24–33. [CrossRef]
- Xiao, X.; Zhang, Y.Y.; Jiang, G.Y.; Liu, J.; Han, S.L.; Zhao, Z.; Wang, R.P.; Li, C.; Xu, C.M.; Duan, A.J.; et al. Simultaneous realization of high catalytic activity and stability for catalytic cracking of n-heptane on highly exposed (010) crystal planes of nanosheet ZSM-5 zeolite. *Chem. Commun.* 2016, 52, 10068–10071. [CrossRef] [PubMed]
- Seo, Y.; Cho, K.; Jung, Y.; Ryoo, R. Characterization of the Surface Acidity of MFI Zeolite Nanosheets by 31P NMR of Adsorbed Phosphine Oxides and Catalytic Cracking of Decalin. ACS Catal. 2013, 3, 713–720. [CrossRef]
- Li, S.; Li, J.; Dong, M.; Fan, S.; Zhao, T.; Wang, J.; Fan, W. Strategies to control zeolite particle morphology. *Chem. Soc. Rev.* 2019, 48, 885–907. [CrossRef]
- Olafson, K.N.; Li, R.; Alamani, B.G.; Rimer, J.D. Engineering Crystal Modifiers: Bridging Classical and Nonclassical Crystallization. *Chem. Mater.* 2016, 28, 8453–8465. [CrossRef]
- Lupulescu, A.I.; Kumar, M.; Rimer, J.D. A facile strategy to design zeolite L crystals with tunable morphology and surface architecture. J. Am. Chem. Soc. 2013, 135, 6608–6617. [CrossRef]
- Lupulescu, A.I.; Rimer, J.D. Tailoring silicalite-1 crystal morphology with molecular modifiers. *Angew. Chem. Int. Ed. Engl.* 2012, 51, 3345–3349. [CrossRef]
- Qin, W.; Agarwal, A.; Choudhary, M.K.; Palmer, J.C.; Rimer, J.D. Molecular Modifiers Suppress Nonclassical Pathways of Zeolite Crystallization. *Chem. Mater.* 2019, 31, 3228–3238. [CrossRef]
- Kumar, M.; Luo, H.; Roman-Leshkov, Y.; Rimer, J.D. SSZ-13 Crystallization by Particle Attachment and Deterministic Pathways to Crystal Size Control. J. Am. Chem. Soc. 2015, 137, 13007–13017. [CrossRef] [PubMed]
- Zhang, Q.; Mayoral, A.; Terasaki, O.; Zhang, Q.; Ma, B.; Zhao, C.; Yang, G.; Yu, J. Amino Acid-Assisted Construction of Single-Crystalline Hierarchical Nanozeolites via Oriented-Aggregation and Intraparticle Ripening. J. Am. Chem. Soc. 2019, 141, 3772–3776. [CrossRef] [PubMed]
- Song, X.; Yang, X.; Zhang, T.; Zhang, H.; Zhang, Q.; Hu, D.; Chang, X.; Li, Y.; Chen, Z.; Jia, M.; et al. Controlling the Morphology and Titanium Coordination States of TS-1 Zeolites by Crystal Growth Modifier. *Inorg. Chem.* 2020, 59, 13201–13210. [CrossRef]
- 34. Emeis, C.A. Determination of integrated molar extinction coefficients for infrared-absorption bands of pyridine adsorbed on solid acid catalysts. *J. Catal.* **1993**, *141*, 347–354. [CrossRef]
- 35. Wang, J.; Shan, J.; Tian, Y.; Zhu, T.; Duan, H.; He, X.; Qiao, C.; Liu, G. Catalytic cracking of n-heptane over Fe modified HZSM-5 nanosheet to produce light olefins. *Fuel* **2021**, *306*, 121725–121735. [CrossRef]
- Vuong, G.-T.; Do, T.-O. A new route for the synthesis of uniform nanozeolites with hydrophobic external surface in organic solvent medium. J. Am. Chem. Soc. 2007, 129, 3810–3811. [CrossRef]
- Liu, J.; Li, Y.; Chen, Z.; Li, Z.; Yang, Q.; Hu, L.; Jiang, G.; Xu, C.; Wang, Y.; Zhao, Z. Hierarchical ZSM-5 Zeolites with Tunable Sizes of Building Blocks for Efficient Catalytic Cracking of i-Butane. *Ind. Eng. Chem. Res.* 2018, 57, 10327–10335. [CrossRef]
- Wei, R.; Yang, H.; Scott, J.A.; Aguey-Zinsou, K.-F.; Zhang, D. Synthesis of 2D MFI zeolites in the form of self-interlocked nanosheet stacks with tuneable structural and chemical properties for catalysis. *Appl. Mater. Today* 2018, *11*, 22–33. [CrossRef]
- Shen, X.; Mao, W.; Ma, Y.; Xu, D.; Wu, P.; Terasaki, O.; Han, L.; Che, S. A Hierarchical MFI Zeolite with a Two-Dimensional Square Mesostructure. *Angew. Chem. Int. Ed. Engl.* 2018, 57, 724–728. [CrossRef]

- Wang, R.; Peng, Z.; Wu, P.; Lu, J.; Rood, M.J.; Sun, H.; Zeng, J.; Wang, Y.; Yan, Z. Direct Synthesis of Nanosheet-Stacked Hierarchical "Honey Stick-like" MFI Zeolites by an Aromatic Heterocyclic Dual-Functional Organic Structure-Directing Agent. *Chemistry* 2021, 27, 8694–8697. [CrossRef]
- Bonilla, G.; Diaz, I.; Tsapatsis, M.; Jeong, H.K.; Lee, Y.; Vlachos, D.G. Zeolite (MFI) crystal morphology control using organic structure-directing agents. *Chem. Mater.* 2004, 16, 5697–5705. [CrossRef]
- Chaikittisilp, W.; Suzuki, Y.; Mukti, R.R.; Suzuki, T.; Sugita, K.; Itabashi, K.; Shimojima, A.; Okubo, T. Formation of hierarchically organized zeolites by sequential intergrowth. *Angew. Chem. Int. Ed. Engl.* 2013, 52, 3355–3359. [CrossRef] [PubMed]
- 43. Zhang, X.; Liu, D.; Xu, D.; Asahina, S.; Cychosz, K.A.; Agrawal, K.V.; Al Wahedi, Y.; Bhan, A.; Al Hashimi, S.; Terasaki, O.; et al. Synthesis of self-pillared zeolite nanosheets by repetitive branching. *Science* **2012**, *336*, 1684–1687. [CrossRef]
- 44. Liu, Y.; Qiang, W.; Ji, T.; Zhang, M.; Li, M.; Lu, J. Uniform hierarchical MFI nanosheets prepared via anisotropic etching for solution-based sub-100-nm-thick oriented MFI layer fabrication. *Sci. Adv.* **2020**, *6*, eaay5993. [CrossRef] [PubMed]
- Chang, A.; Yang, T.C.; Chen, M.Y.; Hsiao, H.M.; Yang, C.M. Hierarchical zeolites comprising orthogonally stacked bundles of zeolite nanosheets for catalytic and adsorption applications. *J. Hazard. Mater.* 2020, 400, 123241. [CrossRef]
- Cychosz, K.A.; Guillet-Nicolas, R.; Garcia-Martinez, J.; Thommes, M. Recent advances in the textural characterization of hierarchically structured nanoporous materials. *Chem. Soc. Rev.* 2017, *46*, 389–414. [CrossRef]
- Liu, B.; Duan, Q.; Li, C.; Zhu, Z.; Xi, H.; Qian, Y. Template synthesis of the hierarchically structured MFI zeolite with nanosheet frameworks and tailored structure. New J. Chem. 2014, 38, 4380–4387. [CrossRef]
- Pérez-Ramírez, J.; Verboekend, D.; Bonilla, A.; Abelló, S. Zeolite Catalysts with Tunable Hierarchy Factor by Pore-Growth Moderators. *Adv. Funct. Mater.* 2009, 19, 3972–3979. [CrossRef]
- 49. Choi, M.; Cho, H.S.; Srivastava, R.; Venkatesan, C.; Choi, D.H.; Ryoo, R. Amphiphilic organosilane-directed synthesis of crystalline zeolite with tunable mesoporosity. *Nat. Mater.* **2006**, *5*, 718–723. [CrossRef]
- Zhang, H.; Ma, Y.; Song, K.; Zhang, Y.; Tang, Y. Nano-crystallite oriented self-assembled ZSM-5 zeolite and its LDPE cracking properties: Effects of accessibility and strength of acid sites. J. Catal. 2013, 302, 115–125. [CrossRef]
- Davis, T.M.; Drews, T.O.; Ramanan, H.; He, C.; Dong, J.; Schnablegger, H.; Katsoulakis, M.A.; Kokkoli, E.; McCormick, A.V.; Penn, R.L.; et al. Mechanistic principles of nanoparticle evolution to zeolite crystals. *Nat. Mater.* 2006, *5*, 400–408. [CrossRef] [PubMed]
- 52. Lin, L.; Qiu, C.; Zhuo, Z.; Zhang, D.; Zhao, S.; Wu, H.; Liu, Y.; He, M. Acid strength controlled reaction pathways for the catalytic cracking of 1-butene to propene over ZSM-5. J. Catal. 2014, 309, 136–145. [CrossRef]
- Lu, J.; Zhao, Z.; Xu, C.; Zhang, P.; Duan, A. FeHZSM-5 molecular sieves—Highly active catalysts for catalytic cracking of isobutane to produce ethylene and propylene. *Catal. Commun.* 2006, 7, 199–203. [CrossRef]
- Jin, F.; Li, Y. A FTIR and TPD examination of the distributive properties of acid sites on ZSM-5 zeolite with pyridine as a probe molecule. *Catal. Today* 2009, 145, 101–107. [CrossRef]
- 55. Zhang, X.; Cheng, D.; Chen, F.; Zhan, X. n-Heptane catalytic cracking on hierarchical ZSM-5 zeolite: The effect of mesopores. *Chem. Eng. Sci.* 2017, 168, 352–359. [CrossRef]
- Gong, T.; Zhang, X.; Bai, T.; Zhang, Q.; Tao, L.; Qi, M.; Duan, C.; Zhang, L. Coupling Conversion of Methanol and C4 Hydrocarbon to Propylene on La-Modified HZSM-5 Zeolite Catalysts. *Ind. Eng. Chem. Res.* 2012, *51*, 13589–13598. [CrossRef]
- 57. Yan, X.; Liu, B.; Huang, J.; Wu, Y.; Chen, H.; Xi, H. Dual Template Preparation of MFI Zeolites with Tuning Catalytic Properties in Alkylation of Mesitylene with Benzyl Alcohol. *Ind. Eng. Chem. Res.* **2019**, *58*, 2924–2932. [CrossRef]
- Schallmoser, S.; Ikuno, T.; Wagenhofer, M.F.; Kolvenbach, R.; Haller, G.L.; Sanchez-Sanchez, M.; Lercher, J.A. Impact of the local environment of Brønsted acid sites in ZSM-5 on the catalytic activity in n-pentane cracking. J. Catal. 2014, 316, 93–102. [CrossRef]
- Xiao, X.; Sun, B.; Wang, P.; Fan, X.; Kong, L.; Xie, Z.; Liu, B.; Zhao, Z. Tuning the density of Brønsted acid sites on mesoporous ZSM-5 zeolite for enhancing light olefins selectivity in the catalytic cracking of n-octane. *Microporous Mesoporous Mater.* 2022, 330, 111621–111635. [CrossRef]
- Xue, Y.F.; Li, J.F.; Wang, P.F.; Cui, X.J.; Zheng, H.Y.; Niu, Y.L.; Dong, M.; Qin, Z.F.; Wang, J.G.; Fan, W.B. Regulating Al distribution of ZSM-5 by Sn incorporation for improving catalytic properties in methanol to olefins. *Appl. Catal. B Environ.* 2021, 280, 119391. [CrossRef]
- 61. Wang, D.; Zhang, L.; Chen, L.; Wu, H.; Wu, P. Postsynthesis of mesoporous ZSM-5 zeolite by piperidine-assisted desilication and its superior catalytic properties in hydrocarbon cracking. *J. Mater. Chem. A* **2015**, *3*, 3511–3521. [CrossRef]
- Xiao, X.; Xu, Z.; Wang, P.; Liu, X.; Fan, X.; Kong, L.; Xie, Z.; Zhao, Z. Solvent-Free Synthesis of SAPO-34 Zeolite with Tunable SiO₂/Al₂O₃ Ratios for Efficient Catalytic Cracking of 1-Butene. *Catalysts* 2021, *11*, 835. [CrossRef]
- 63. Arudra, P.; Bhuiyan, T.I.; Akhtar, M.N.; Aitani, A.M.; Al-Khattaf, S.S.; Hattori, H. Silicalite-1 As Efficient Catalyst for Production of Propene from 1-Butene. ACS Catal. 2014, 4, 4205–4214. [CrossRef]