

Synergism of Titanium in MFI Zeolite to Acidity with Its Appliance to N-Hexane Catalytic Cracking Reaction

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Abstract

Catalytic cracking of naphtha is now a process of huge development potential to produce light olefins, which are important basic raw materials used in various industries, but current industrial catalysts like ZSM-5 zeolites suffer from low selectivity and high energy consumption. Here, Ti/Al-containing nanosize MFI-structure zeolites in-situly synthesized through one-pot method were applied to the catalytic cracking using n-hexane as the model reactant. The maximum mass yield of combined light olefins reaches 49.2% with 99% conversion at 600°C and 1 atm. Multiple characterizations are used to identify the Ti-related active species and their effect on the performance. It was found that a higher proportion of LAS caused by Ti was beneficial to the activation of reactant, and the slightly increased amount of BAS leaded to more alkanes converting into light olefins. This understanding may open new opportunities for design and modification of catalytic cracking catalysts.

Keywords

Catalytic Cracking, Light Olefin, MFI Zeolite, Titanium

1. Introduction

Light olefins are among the most crucial chemicals for modern industry. More and more attention has been focused on the development of related techniques due to the increasing demand. At present, light olefins are mainly acquired via naphtha cracking [1] [2], low carbon alkane dehydrogenation [3], and coal/methanol to olefins [4]. Among these, the naphtha route is more suitable for large-scale production benefiting from easily accessible resources and low oil prices. However, traditional steam cracking process of naphtha has series of disadvantages like high energy consumption, low return to investment ratio and uncontrollability of products distribution [5] [6]. Catalytic cracking process utilizing catalysts offers an opportunity to solve the above-mentioned problems.

Up to now, zeolites are the most commonly used catalysts in naphtha catalytic cracking [7], especially the ZSM-5 zeolite with moderate solid acidity and threedimensional channel structure [8]. Besides, its excellent thermal stability and reproducibility are also useful considering the severe reaction conditions. However, conventional ZSM-5 was confronted with problems of low selectivity of olefin in catalytic cracking. Hence, many studies have focused on the optimization of activities to regulate its catalytic performances, like post-treatment, metal deposition, hierarchical structure, which usually need extra procedures [6] [9].

To solve the above-mentioned problems, nanosized MFI zeolites with different titanium and alumina contents have been successfully synthesized through one-pot method in this work. Characterization methods like XRD, SEM, N_2 -absorption and desorption, NH_3 -TPD, FT-IR, UV-DRS and UV-Raman were employed to identified textural properties, acidity and the structure feature. Besides, the catalytic cracking performance of naphtha was clarified by using n-hexane as the model reactant.

2. Experimental

2.1. Preparation of Catalysts

The parent ZSM-5 zeolite (Si/Al = 120, named as PZ) was obtained using tetrapropylammonium hydroxide (TPAOH, 25% aqueous solution, Alfa Aesar), tetraethyl orthosilicate (TEOS, 98%, Sigma), Sodium aluminum oxide ($Na_2Al_2O_4$, 98%, Macklin) as raw materials. The gel with the molar composition 1.0 SiO₂: 0.00416 $Na_2Al_2O_4$: 0.35 TPAOH: 25 H₂O was stirred at 25°C for 3 h and then heated at 86°C to remove ethanol generated during the hydrolysis of TEOS and then deionized water was added to maintain a constant volume [10]. Finally, the gel was moved into a Teflon-lined stainless steel autoclave, and crystallized at 180°C for 72 h. The Silicate-1 sample has the same molar gel with that of PZ except none of Sodium aluminum oxide.

The MFI structure zeolite containing Titanium (Si/Al = 120, named as TZ-y, y = 1, 3, 5, where "y" refers to the molar composition "x" of titanium in following gel) were obtained using same material of PZ, besides Titanium(IV) butoxide (97%, Sigma-Aldrich) and Isopropanol (AR, Greagent) using as Titanium source and diluent. The gel with molar composition 1.0 SiO₂: 0.00416 Na₂Al₂O₄: xTiO₂ (x = 0.0077, 0.0231, 0.0385): 0.35 TPAOH: 25 H₂O: 4.36 Isopropanol went through the same process of PZ. The TS-1 sample has the same molar gel with that of TZ-1 except none of Sodium aluminum oxide.

All of these samples were then filtered, flushed using deionized water, and dried at 110°C for 12 h. To ensure removal of OSDAs, the samples were calcined at 550°C for 6 h. The H-type zeolite was obtained by ion exchange method using

 $1 \text{ M NH}_4\text{NO}_3$ solution with the solid/solution mass ratio of 1:30 at 80°C for 12 h. This process was repeated three times to ensure that most sodium ions were removed.

For comparison, the industrial H-type ZSM-5 zeolite (Si/Al = 120, named as IZ) was getting from Nankai University Catalyst Co., Ltd (Tianjin, P.R. China).

2.2. Characterization

Powder X-ray diffraction (XRD) patterns was conducted on a Bruker D8-Advance with monochromatized Cu K α radiation (20 kV and 5 mA) over 2 θ range between 5° and 50°, the relative crystallinity of the samples was calculated by comparing the sum of the peak intensity at 2 θ of 7.9°, 8.7°, 23.1°, 23.9° and 24.4° of samples with that of PZ defined as 100%. Scanning electron microscopy (SEM) images were employed to detect the morphology of different samples on a FEI Nova NanoSEM 450 at 3 kV. Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) was employed on an Agilent 725 spectrometer. Surface area and pore size analysis was measured on a Micromeritics ASAP2020 instrument. In a typical test, ~100 mg sample was degassed at 300°C for 12 h prior to the exposure to liquid Nitrogen. From the N₂ adsorption-desorption isotherm, Specific surface area (S_{BET}), external surface area (S_{EXT}) were calculated using Brunauer-Emmett-Teller (BET) equation in the 0.15 - 0.28 relative pressure range, and pore volumes were calculated using Barrett-Joyner-Halenda (BJH) model [11].

Temperature programmed desorption of ammonia (NH₃-TPD) was employed to detect the strength and amount of acid sites on catalysts, and carried out on a Micromeritics ASAP2720 fitted with a thermal conductivity detector. In a typical test, ~100 mg sample was pretreated in the quartz tube at 500°C under He flow for 1 h. then it cooled to 35°C, 10% NH₃/He was introduced at a flow rate of 20 mL/min for 0.5 h, followed by flowing He at 120°C until constant TCD signals were obtained to ensure all reversibly and physically bound ammonia being removed. Then the measurement was carried out from room temperature to 700°C with a heating rate of 10°C/min under Heat a flow rate of 20 mL/min. The number of acid sites was determined from the peak area [12], then quantitative data is obtained from the calibration curve.

FT-IR spectra were recorded on a Thermo Fisher Nicolet IS50 spectrometer to obtain the characteristic peak of samples. Self-supporting wafers with a mass ratio of 1:80 for the sample and KBr mixture were prepared [13]. The spectrum was collected at room temperature in air at 0.482 cm⁻¹ resolution. Pyridine adsorbed infrared spectra (Py-IR) was employed to distinguish the acid type on zeolites [14], and obtained with a CaF_2 window and vacuum system at 0.482 cm⁻¹ optical resolution. All samples were pressed to sheets (around 15 mg, 13 mm of diameter) before placing them in the sample cell. The sample was pretreated at 480°C for 2 h under vacuum to remove the adsorbed species, then cooled down to 250°C and 130°C in sequence to record corresponding background spec-

trums. Then the sample was exposed to pyridine at room temperature until saturation. Finally, spectrums were recorded after vacuum treatment for 1 h at 130° C and 250° C, respectively.

Room temperature UV-vis diffuse reflectance spectroscopy (UVDRS) was conducted on a Perkin-Elmer Lambda 750 UV-vis-NIR spectrophotometer using a labsphere accessory over the range of 190 - 400 nm.

UV Raman spectrum was recorded on a Renishaw invia reflex laser Micro-Raman Spectrometer. A 325-nm line of He–Ge laser was used as the excitation sources.

Catalytic Tests

The performance of catalyst was tested in a fixed-bed quartz reactor system using n-hexane as a model reactant for light naphtha. According to the size of the reaction tube, 0.6 g samples was set in the stationary temperature center (temperature fluctuation ≤ 0.5 °C) of the reactor. The weight hourly space velocity (WHSV) was 1 h⁻¹, and carrier gas (N₂) flow rate was 9 sccm. Before the reaction, sample was heated by carrier gas at 550 °C for 2 h and then reacted at 0.1 MPa for 5 h. The outlet product was heated to 110 °C to avoid condensation, and quantitatively analyzed every 60 min on an Fuli 9790 II gas chromatography equipped with an Agilent J & W PoraPLOT Q-HT (25 m * 0.53 mm * 20 µm) capillary column.

To obtain the result, the equivalent mole fraction in product, x_{ρ} the mass yield, Y_i and conversion of n-hexane, α_{nCb} are given by the following formulae;

$$x_{i} = A_{i} \times \frac{x_{i,0}}{A_{i,0}}$$

$$Y_{i} = \frac{x_{i} \times W_{i}}{\sum x_{i} \times W_{i}} \times 100\%$$

$$\alpha_{nC6} = \frac{Hexane_{in} - Hexane_{out}}{Hexane_{in}} \times 100\%$$

where A_i is the peak area of species *i* getting from GC, W_i is the molecular weight of species *i*, x_p 0 and A_p 0 are the equivalent mole fraction and peak area of species *i* about the standard gas sample.

3. Result and Discussion

3.1. Textural and Morphology Properties

XRD pattern of different sample are shown in **Figure 1** to confirm the structure of samples. There are six typical peaks at 8.0°, 8.9°, 23.2°, 23.7°, 24.0° and 24.4°, corresponding to characteristic of MFI structure zeolite (JCPDS #044-0003) and the relative crystallinity is listed in **Table 1**. The diffraction peaks were sharp and intense, indicating their well crystalline nature. No characteristic of Ti species are observed presumably because of its low content, good dispersion or the well crystallinity of zeolite framework. Besides, the crystallinity order of all samples is PZ \approx TZ-1 >> Silicate-1 > TS-1 \approx TZ-3 > TZ-5. It can be found that the crystallinity



Figure 1. XRD pattern of the catalysts.

Sample	relative crystallinity	Si/Al	Ti (%)	S _{BET} (m²/g)	S _{EXT} (m²/g)	V _{total} (ml/g)	V _{micro} (ml/g)
PZ	100%	122	-	382	53	0.31	0.18
Silicate-1	67%	-	-	351	135	0.38	0.12
TS-1	48%	-	0.60	406	233	0.37	0.12
TZ-1	101%	116	0.58	409	310	0.48	0.16
TZ-3	47%	123	1.82	370	214	0.47	0.14
TZ-5	44%	118	2.79	397	217	0.49	0.11

Table 1. Texture properties of the catalysts.

of Al-containing samples will be significantly improved comparing with samples without Al, while the other synthesis conditions stay the same. This is owe to the charge effect where the negatively charged precursor with the addition of Al can form closer interaction with the positively charged TPA⁺ ions in the solution, making it plays a better space filling role as structure directing agents, and finally resulting in the higher crystallinity. On the other side, the excessive addition of titanium in the sample will decrease the crystallinity which results from the lattice distortion caused by the framework Ti atoms with larger radius [15] [16]. With the combination of above two, the crystallinity difference of samples can be well explained.

To study the morphology of catalysts, SEM images were shown in **Figure S1**, in which the PZ and TZ-y (y = 1, 3, 5) all showed a cubic or spherical crystal with the crystal sizes of ~150 nm, and samples with higher relative crystallinity have smoother crystal surfaces.

ICP-AES is employed to detect the real element content and its distribution, respectively. The Si:Al ratio and Ti content of samples roughly match with that of the sol for synthesis.

 N_2 adsorption-desorption isotherms of samples are shown in Figure S2 and the corresponding data are summarized in Table 1. All samples show the steep increase in the N_2 uptake at the low relative pressures of $P/P_0 < 0.01$, confirming the presence of micropore, which is the main character of representative type-I

curves considered to be responsible for microporous adsorbents. Besides, all self-made samples show small type H_2 hysteresis loops and steep increase in their adsorption curves at $P/P_0 > 0.9$, which are attributed to the filling of intercrystalline voids.

The textural properties show that the specific surface area of samples are around 400 m²/g and the micropore volumes vary from 0.11 to 0.18 cm³/g, which is consistent with the variation of relative crystallinity obtained from XRD. These results indicate that all samples are mainly microporous material, which could provide enough surface area for catalytic cracking reaction, contributing to revealing the nature of different catalysts.

3.2. Structural Features of Ti Species

Now that Ti has been introduced into the samples, the structure of Ti species needs to be evaluated. Considerable research efforts have been devoted to the titanium silicalite. But when it comes to MFI structure zeolite which contains both titanium and alumina, few systematic studies has been published yet. To further explore the structural feature of Ti species, FTIR, UVDRS spectra and UV Raman spectra are showed in **Figures 2-4**, respectively.



Figure 2. FT-IR spectra of the catalysts.







Figure 4. UV-Raman spectra of the catalysts.

All samples have similar FT-IR spectra, except for the characteristic absorption peak of the TS-1 and TZ-1, 3, 5 appears at 960 cm⁻¹, which is thought to be closely related to the stretching vibration of framework Si-O bands affected by the vicinal Ti atoms [17]. The intensity of this signal increases to a certain extent with the increase of titanium content and keep relatively stable. It can be concluded that the Ti content in the zeolite framework has reached approximately saturation according to Beer-Lambert Law [18].

As shown in Figure 3, the UVDRS spectra of samples show three main absorption bands at nearly 210 nm, 240 nm and 320 nm which can be assigned to the framework Ti species, amorphous Ti species, and anatase [19] [20], so that of PZ and Silicate-1 samples shows none of them. As compared with that of TS-1, the 320 nm absorption band of TZ-1 has almost disappeared. Furthermore, all three absorption bands of TZ-1, 3, 5 are significantly enhanced with the increasing Ti content. On the basis of these results, it can be concluded that the framework tetracoordinated Ti species and nonframework amorphous Ti species are present in all Ti-MFI structure samples, and the introduction of aluminum to the precursor sol inhibits the formation of anatase to an certain extent during the crystallization of zeolites under the premise of the same titanium content. Besides, the content of anatase increases significantly faster than that of framework titanium and amorphous titanium species with the increase of Ti content, this may cause by the threshold of Ti in the precursor sol [21]. The excessive Ti directly generates titanium dioxide at the early hydrolysis process and finally converts into anatase after calcination, which has been verified in previous literature reports.

The UV Raman spectra of TS-1 samples excited by the 325 nm line are shown in **Figure 4**. It can be observed that all samples show the peaks at 294, 380 and 475 cm⁻¹ which are assigned to the 6, 5 and 4 member-ring basic unit of the MFI structure zeolites [22]. The peak at 960 and 1125 cm⁻¹, which can be related to the framework Ti species, are observed in all Ti-containing samples [23]. The TS-1, TZ-3, TZ-5 samples have the clear peaks at 142, 514 and 635 cm⁻¹ assigned to the character of anatase [24], whose intensity increase with the Ti content, while this peak is not observed in TZ-1. It can be conclude that the formation of anatase increases with the increase of titanium content, and the addition of aluminum can inhibit the formation of anatase to a certain extent, which is consistent with the result getting from UVDRS spectra. On the other side, the TS-1 sample has several bands at around 700 cm⁻¹, which can be assigned to the symmetric vibration of hexacoordinated Ti-O-Ti [25]. Although the UVDRS spectra shows the existence of nonframework amorphous Ti species, the bands at 700 cm⁻¹ is not observed in TZ-1, TZ-3 and TZ-5. Further comparing the spectra, we find that the peaks at 830 and 960 cm⁻¹ of these three samples are enhanced, which can be assigned to nonframework Ti monomer like TiO₆ or TiO₅ (isolated by SiO₄ or AlO₄). Based on this finding, it can be indicated that the process of their transformation into amorphous species, and the distribution of Ti atoms more uniform.

3.3. Acidity

The acidity of zeolite catalysts is a very important chemical property for catalytic cracking reaction of hydrocarbon. So far, the most titanium silicate is used for selective epoxidation reaction of hydrocarbon because of the high-activity framework tetrachordinate Ti center [26] [27]. As acidity can depress the activity and selectivity of epoxidation reaction, much work has focused on eliminating the harmful effect caused by the acidity of titanium silicate [28] [29]. Further effort is required to understand how to enhance or better control the acidity of Ti-MFI structure zeolite through the coordination of Al and Ti.

The NH₃-TPD profiles of samples are shown in **Figure 5** to compare the density and strength of the acidity, and the corresponding data are listed in **Table 2**. Each sample has two distinct NH₃ desorption peaks owing to the weakly adsorbed and strongly bounded NH₃, respectively [30]. Otherwise, all samples own the similar acid density and strength at both weak and strong acid sites, which are highly consistent with the same crystal structure and the close Si/Al ratios of the zeolites except TS-1 shows much lower acidity. When comparing PZ and TZ-1, 3, 5, it can be seen that when the Ti content increase to 1%, the weak acid amount decrease and the strong acid amount increase, relatively; if continue to increase the Ti content to 3%, the weak acid amount rises to slightly higher than

Sample	Total acidity (μmol/g)	Weak/strong %	130°C B:L	250°C B:L
PZ	175	28.7:71.3	1.000:1.416	1.000:0.183
TS-1	55	39.4:60.6	1.000:417.7	1.000:0.250
TZ-1	159	24.2:75.8	1.000:3.156	1.000:0.118
TZ-3	238	26.0:74.0	1.000:2.636	1.000:0.189
TZ-5	209	24.0:76.0	1.000:7.671	1.000:0.089

Table	2. /	Acidity	of	of	the	cata	lysts
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Figure 5. NH₃-TPD curves of the catalysts.

that of PZ and the strong acid amount significantly increases to a peak value. However, both weak and strong acid amount decreases to a certain extent when the Ti content keep increase to 5%. Otherwise, the weak acid and strong acid ratio of TZ-1, 3, 5 is lower than that of PZ. These results suggest that Ti can provide acidity to zeolites even without the presence of Al, and the addition of an appropriate amount of Ti can significantly increase the strong acid amount in the case of a certain amount of Al in zeolites. However, too little or too much Ti will cause the by-effect of decreasing the weak acid amount.

Since the size of the pyridine molecule is within that of micropores in MFIstructure zeolites, it is an ideal probe molecule to determine the concentration of Lewis and Brønsted acid sites (LAS and BAS). Generally, Py-IR spectrums of samples give four peaks at around 1450, 1485, 1540 and 1600 cm⁻¹. The band at 1540 and 1485 cm⁻¹ is assigned to the pyridinium ions formed by pyridine adsorbed on BAS, and the band at 1450, 1485 and 1600 cm⁻¹ results from coordinated pyridine on LAS [31] [32] [33]. The ratio of BAS and LAS are calculated using the peak area at 1540 and 1450 cm⁻¹, respectively, and summarized in **Table 2**.

As shown in **Figure 6**, all samples show the characterization of BAS and LAS after treated at 130°C except TS-1. A number of previous studies have provided strong evidence for the presence of LAS on titanium silicate, and it is generally accepted that the tetracoordinated Ti sites in the MFI framework have Lewis acidity. It is noteworthy that the bands at 1600 cm⁻¹ of all Ti containing samples apparently shifted to high wavenumber, which indicates that the C = N bond of pyridine coordinated with LAS is affected by the change of chemical environment [34]. It can be owing to the conjugation effect between pyridine and neighboring framework Ti. On the other hand, uncertainty still remain as to the



Figure 6. Py-IR spectra of the catalysts.

existence of BAS on it. The band of the TS-1 sample at around 1540 cm⁻¹ seems not obvious. However, comparing the spectrums of samples, together with Table 2, it can be seen that the introduction of Ti provides certain amount of LAS. With the treating temperature increase from 130°C to 250°C, it can be seen that the peak at 1450 cm⁻¹ all rapidly decrease and that of TZ-1, 3, 5 decrease more. It is widely accepted that BAS are generally strong acid sites, while LAS are mainly weak acid sites. Considering the acidity of anatase can be neglected, these characterizations, together with the results from UVDRS and UV-Raman, strongly support that the enhancement of acidity is probably due to the formation of the amorphous Ti species. The amorphous Ti species in samples should be equal to the heterogeneous TiO₂-SiO₂-Al₂O₃ binary mixture, the coordination number of Ti^{4+} , Si^{4+} can be 6 and 4, while that of O^{2-} can be either 2 or 3 [35]. Beside, some studies demonstrated that the coordination number of Al^{3+} can be 4, 5 or 6 [36]. In any case of combination, the binary mixture will have excessive charge. When the charge is positive, the mixture needs electron to keep neutral, which shows the character of LAS. When the charge is negative, the mixture should have extra H^+ and displays BAS. This tendency is in good agreement with the NH_3 -TPD measurements which can explain why the TZ-5 has the lowest relative crystallinity among all the sample but with highest acidity.

3.4. Catalytic Performance

The mechanism of catalytic cracking is generally regarded as can be divided into two parts. When the reaction temperature is low (below 550°C), carbonium ion mechanism and mono-bimolecular mechanism play dominant roles. With the increase of temperature (>600°C), free radical mechanism becomes evident [37]. To evaluate the catalytic performance, the reaction under 600°C was completed at first. After the data were summarized, the reaction at 500°C was also done to amplify the influence of Ti modification and eliminate the effect of thermal cracking as much as possible. The catalytic cracking performance of n-hexane is presented in **Figure 7**.

At 600°C, the initial conversions for PZ, TZ-1, 3, 5 all reached around 99%, while that of S-1 and TS-1 were 44.1% and 53.2%. This result shows that appropriate



Figure 7. Catalytic performances of the catalysts at 600°C (Upper) and 500°C (bottom).

amount of acid sites provided by the framework Al atoms is essential to activate reactants. Otherwise, the introduction of Ti actually could improve the conversion of n-hexane for about 9%, comparing to that of Silicate-1. This phenomena is mainly because of the extra LAS on the TS-1 sample comparing to that of Silicate-1. According to the carbonium ion mechanism [38], alkane reactants transfer H⁻ to LAS on the catalyst at the beginning of the reaction, and then change into carbonium ions, which undergo further reaction such as isomerization, β -secession, hydride transfer and cyclization. This finally results in the increasing conversion of the TS-1 sample.

As the main products in catalytic cracking, the combined mass yield of light olefin (include ethylene, propylene, butane and butadiene) is also taken to evaluate the catalytic performance. The TZ-3 sample has the highest one of 49.2%, displaying the yield of 4.9%, 3.3% and 2.2% higher than that of PZ, TZ-1 and TZ-5, respectively. The mass yield of light olefin for Silicate-1 and TS-1 is much lower, but when taking their conversion into consideration, their selectivity of light olefin are about 67%, higher than anyone else. Since their morphologies and texture properties are similar, it can be concluded that the high olefins yield of TZ-3 sample is related to its higher acidity, and more reactants occur the fracture of C-C bonds with the dehydrogenation to generate olefins [39]. On the

other side, the Silicate-1 and TS-1 sample lack BAS provided by the framework Al atoms, which result in the lower conversion of n-hexane but high selectivity of light olefins.

The mass yield of byproducts is also is a noteworthy issue (that of hydrogen is around 0.5%, so there will not be further discussion about it). Due to the thermodynamic stability of methane which makes it hard to be further converted, low methane yield is preferred. For PZ and TZ-1, 3, 5 samples, the methane yield of PZ is slightly higher than that of other samples, the coordination of Ti and Al may enhance the activation of short linear alkanes by strong BAS on catalyst. This conclusion can also be supported by the relatively high methane yield (considering the n-hexane conversion) of the Silicate-1 and TS-1 sample where the lack of BAS can hardly protonate methane to generate nonclassical carbonium ions which can re-participate in the reaction [40].

When the reaction temperature comes to 500°C, there is a difference in the conversion of n-hexane for samples. PZ sample has the highest one of 97%, and that of TZ-1, 3, 5 are 86.6%, 82.6%, 88.3%, respectively. Besides, the tendency of light olefin mass yield for these four samples agrees with their difference in acidity getting from NH₃-TPD and Py-IR. The conversion of TZ-1, 3, 5 and the ratio of BAS to LAS show a negative correlation under this lower temperature which proves that LAS plays a critical role in the initiation activation step. At the same time, the yield of methane and aromatics decreases as the temperature goes down, combined paraffin become the main byproduct, which leads us to conclude that the initial intermediates mainly transform into propylene and $C_3H_7^+$ ions through β -secession, meanwhile, the reaction speed of dehydrogenation and hydride transfer is low [41]. Most of $C_3H_7^+$ ions regained H⁻ from the catalyst and generated more stable propane. However, the TZ-3 sample with more BAS gets the lowest yield of propane with the highest yield of propylene, which can be attributed to the attack of BAS to the light alkane. On the basis of our finding, it can be concluded that the change in acidity caused by Ti species is a key factor affecting the products yield of Ti/Al-containing MFI structure zeolites.

4. Conclusion

In summary, nanosized MFI-structure zeolite with different content of alumina and titanium for naphtha catalytic cracking was investigated. Characterizations like XRD, N₂-absorption, and SEM show samples have a well crystalline structure with similar textural properties and morphology. The main difference is the acidity change caused by the introduction of Ti-related species and the extra BAS and LAS can activate more alkanes which cause the combined olefins mass yield to increase. By far many kinds of materials have been used as the catalysts for naphtha catalytic cracking, yet few studies report the Ti/Al-containing MFI zeolites. It is worth further exploration that whether there is deeper interaction between the Ti sites and the intermediate or not. This may provide some inspiration for the development of new catalysts.

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Conflicts of Interest

The authors declare no competing financial interest.

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Appendix





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Figure S2. N₂ adsorption-desorption isotherms of samples.