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Effects of ZSM-5 Preparation Conditions on Textural Properties and Catalytic Cracking of n-Hexane

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ABSTRACT

In this study, the effects of crystallization temperature, crystallization time, and pH value on the textural properties of synthetic ZSM-5 were investigated by the orthogonal test method. Furthermore, the effects of ZSM-5 catalysts synthesized under different preparation conditions on their reactivity during catalytic cracking were evaluated. Moreover, the results have shown that the three factors that affect the ZSM-5 synthesis are in the following order: crystallization temperature > crystallization time > pH value. In addition, the optimal conditions for synthesizing ZSM-5 catalysts were crystallization temperature of 170 °C, crystallization time of 48 h, and pH of 11. Furthermore, under these conditions, the specific surface area, pore-volume, and acidity of the synthetic zeolite were moderate, and the hydrothermal stability was ideal. Finally, when the optimal conditions were applied to the catalytic cleavage of n-hexane, the synthesized zeolite exhibited good activity and stability.

Keywords: Orthogonal Test, ZSM-5 Zeolite, Preparation Conditions, n-Hexane, Catalytic Cracking.

INTRODUCTION

At present, the global demand for low-carbon olefins is increasing; however, the existing olefin supply does not meet this demand. Approximately, 90% ethylene and 57% propylene are produced by steam cracking in tubular furnaces, which they requires high temperatures between 800 and 1200 °C. The remainder is produced by heavy oil hydrocracking, followed by $C_{6–10}$ light oil catalytic cracking to obtain low-carbon olefins, which requires reaction temperatures between 340 and 420 °C. These two methods are conducted under high-temperature or high-pressure conditions, resulting in high cost and energy consumption as well as increased risks associated with high reaction pressures [1]. However, with a suitable catalyst, the distribution of the cracked products can be altered with an increase in the yield of low-carbon olefins while energy consumption is reduced greatly.

In recent years, a deep catalytic cracking (DCC) process has been developed by the Sinopec Research Institute of Petrochemical Technology [2]. In addition, in deep catalytic cracking process, a solid acid shape-selective zeolite catalyst and

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heavy oil as a raw material to produce low-carbon olefins through a cracking reaction under milder conditions are used. The total mass yield of ethylene, propylene, and butene is 33.54%, but product separation is difficult because of the large volume of by-products. Moreover, ZnAPO-5 with different amounts of zinc were made by using a hydrothermal synthesis method by Feng et al [3], and then synthesized ZnAPO-5 zeolites were applied to the cracking of n-hexane. The conversion rate increased with an increase in the reaction temperature and time; however, reaction activity was low. Furthermore, MoO_2 as a catalyst for the cracking of n-hexane was used by Song et al [4], and a total conversion rate of approximately 100% was achieved. However, because carbon was easily deposited on the MoO_2 layer surface, the selectivity of ethylene and propylene had been only 29% and 35% respectively. Moreover, an MCM-22 precursor catalyst for the dealuminization of HNO_3 was used by Wang et al [5], and the obtained DMCM-22 catalyst had acid volume and stability identical to those of HZSM-5. However, when DMCM-22 was applied to the catalytic cracking of n-hexane and reaction temperature was low, protonic acid had not been activated, resulting in low catalytic activity. At the optimum reaction temperature of 923 °K, the selectivity of propylene was reached 41%, but the carbon deposition resistance was poor. Therefore, it can be deduced by us that an improved catalyst has been crucial for increasing the yield of the cracking reaction. Moreover, most cracking catalysts which have been reported in the literature have disadvantages such as long diffusion path, poor hydrothermal stability, and poor carbon deposition resistance. To overcome these problems, the development of a new type of catalyst with exceptional physicochemical properties is urgently required.

ZSM-5 zeolites are catalysts with a unique three-dimensional pore structure. Because of their large specific surface area, suitable acid volume, and high hydrothermal stability, ZSM-5 catalysts achieve good hydrocarbon catalytic cracking and carbon deposition resistance. Also, HZSM-5 was synthesized by Farzi et al [6], and then HZSM-5 was applied to the cracking reaction of alkanes with Mn modification. Moreover, it was found out by Farzi et al that the selectivity of propylene was positively correlated with temperature; however, the preparation cost of the catalyst was high. Moreover, ZSM-5 was synthesized from kaolin by Mohiuddin et al [7], and then the effects of kaolinite content, crystallization temperatures, and time on the selectivity of gasoline were investigated by them. However, there are many studies on the preparation of ZSM-5 [8-10], the effects of the zeolite preparation conditions on crystallinity, pore structure, acidity, and acid strength have not been systematically evaluated.

Moreover, different physicochemical properties of ZSM-5 can be achieved under different preparation conditions. In particular, crystallization temperature, crystallization time, and pH value were found to be the main factors which affected the physicochemical properties of ZSM-5 [11]. In general, the crystallization temperature affects the polymerization degree of silicate ions in the catalyst pore walls, the pore structure of the catalyst, and the micelles formed by surfactant molecules. Moreover, varying the crystallization time leads to different growth states of the crystal structure during the synthesis. As the crystals continue to grow with time, the pressure inside the crystallization kettle increases; and thereby, the density of the crystal skeleton is increased. Moreover, pH value affects the polymerization degree of silicate ions; therefore, adjusting the pH to an appropriate value will increase the thermal and hydrothermal stabilities of the zeolite catalyst [12]. Consequently, for determining the potential of ZSM-5 in the reaction of alkanes, it is necessary that its preparation conditions be optimized. In this study, the effects of the crystallization temperature, crystallization time, and pH value on the textural properties of synthetic ZSM-5 were investigated by the orthogonal test method. As there are many C6 components in hydrocarbons obtained from heavy oil cracking, the effects of the ZSM-5 catalysts synthesized under different preparation conditions on the conversion of n-hexane during catalytic cracking have been investigated. Moreover, the selectivity and yield of ethylene and propylene were evaluated using a small fixed bed reactor. Thus, the suitability of various textural properties of ZSM-5 for catalytic cracking reactions was characterized, and the optimal conditions for the synthesis of ZSM-5 for the n-hexane cracking reaction were determined. Finally, in this study, it is expected that these findings will provide basic data for the selection and preparation of catalysts for deep cracking of alkanes to produce low-carbon olefins.

EXPERIMENTAL PROCEDURE

Reagents

Sodium metaaluminate (Al_2O_3 = 43%), sodium hydroxide, and ammonium nitrate were all analytically pure (Sinopharm Chemical Reagent Co., Ltd.). Other reagents included silica sol (SiO_2 = 31%, industrial products, Qingdao Ocean Chemical Co., Ltd.), tetrapropylammonium bromide (TPABr, Aladdin Biochemical Technology Co., Ltd.), and deionized water.

Synthesis of ZSM-5

The molar ratio of the reactants was $40SiO_2$: Al_2O_3: 3.5TPABr: xNaOH: yH_2O, and alkalinity was controlled by varying x and y. Moreover, sodium metaaluminate (0.297 g) was dissolved in 16.5 mL of deionized water, followed by dropwise addition of 10 g of silica sol under stirring for 0.5 h to produce solution A. A series of liquid solutions with different pH values were obtained by adding a certain amount of sodium hydroxide and 0.96 g TPABr to solution A. Afterwards, each liquid solution was stirred evenly for 2 h to obtain a uniform sol. Finally, the uniform sol was placed in a stainless steel crystallization kettle, aged at 40 °C for 6 h, and then heated to a certain temperature. After crystallization for a certain time and cooling to room temperature, the filter cake obtained by suction filtration was washed until neutral. The filter cake was dried overnight at 100 °C to obtain a Na-ZSM-5 raw powder, which was then was placed in a muffle furnace and calcined at 550 °C for 5 h to remove the templating agent. The calcined catalyst was further dissolved in ammonium nitrate (1 mol L^{-1}) at 1:30 (g mL^{-1}) and used for ion exchange at 80 °C for 2 h. The catalyst was then washed, dried, and calcined in a muffle furnace at 550 °C for 4 h to remove NH_3. The exchange procedure was repeated three times to obtain the H-ZSM-5 catalyst.

Orthogonal Test Design

The effects of different preparation conditions on the pore structure of the synthesized ZSM-5 zeolites were investigated by the orthogonal test method using the test parameters listed in Table 1 [13].

Table 1: L_{16} (4^3) orthogonal test table for synthesis of ZSM-5 zeolites under various preparation conditions (Sheng-tao QU, Dong-mei LIU, Xin SHI, Hai-yan WANG, and Xin WANG, Effects of ZSM-5 Preparation Conditions on Textural Properties and Catalytic Cracking of n-Hexane).

Sample	Temperature	Time	pH	Combination
HZ-130-12h-11	1	1	1	$A_1B_1C_1$
HZ-130-24h-12.5	1	2	4	$A_1B_2C_4$
HZ-130-48h-11.5	1	3	2	$A_1B_3C_2$
HZ-130-72h-12	1	4	3	$A_1B_4C_3$
HZ-150-12h-12.5	2	1	4	$A_2B_1C_4$
HZ-150-24h-11	2	2	1	$A_2B_2C_1$
HZ-150-48h-12	2	3	3	$A_2B_3C_3$
HZ-150-72h-11.5	2	4	2	$A_2B_4C_2$
HZ-170-12h-11.5	3	1	2	$A_3B_1C_2$
HZ-170-24h-12	3	2	3	$A_3B_2C_3$
HZ-170-48h-11	3	3	1	$A_3B_3C_1$
HZ-170-72h-12.5	3	4	4	$A_3B_4C_4$
HZ-190-12h-12	4	1	3	$A_4B_1C_3$
HZ-190-24h-11.5	4	2	2	$A_4B_2C_2$
HZ-190-48h-12.5	4	3	4	$A_4B_3C_4$
HZ-190-72h-11	4	4	1	$A_4B_4C_1$

Table 1 is a three-factor four-level orthogonal experimental table, in which crystallization temperatures 1, 2, 3, and 4 correspond to 130, 150, 170, and 190 °C respectively. Crystallization times 1, 2, 3, and 4 correspond to 12, 24, 48, and 72 h, respectively; in addition, pH values 1, 2, 3, and 4 correspond to 11, 11.5, 12, and 12.5 respectively. In the horizontal combinations, A, B, and C correspond to the crystallization temperature, crystallization time, and pH respectively.

Physicochemical Characteristics of ZSM-5

The crystal phase structures of the catalyst samples were evaluated using an R-and-D D/max-RB X-ray diffractometer with CuKα radiation (λ = 0.15406 nm, 40 kV, 100 mA), a goniometer radius of 185 mm, and an optical system with slit settings of divergence = scattering = 1° and receiving = 0.15 mm. The morphologies of the samples were observed through scanning electron microscopy (JSM-5610LV). The N_2 adsorption-desorption isotherms of the samples were obtained using a Micromeritics ASAP-2010 adsorber. Moreover, the acid strengths and relative acid volume of the catalysts were analyzed by ammonia temperature-programmed desorption (NH_3-TPD) with a Micromeritics AutoChem 2920 fully automated temperature-programmed chemical adsorption instrument. The pyridine infrared (Py-IR) spectra of the samples were collected using a Bruker Vector 22 infrared spectrometer. The catalyst was treated under high vacuum at 450 °C for 30 min. After the temperature of the quartz absorption cell was lowered to room temperature, the catalyst was allowed to adsorb pyridine for 30 min under static conditions. Subsequently, after maintaining the catalyst sample at 400 °C for 30 min under vacuum, it was cooled to 25 °C, and the Py-IR spectrum was recorded.

Catalytic Cracking of n-hexane

Using n-hexane as the starting material, the catalytic cracking reaction was conducted in an MY-GDC fixed-bed microreactor. The reaction tube was made of stainless steel and had an inner diameter of 10 mm. The catalyst was tableted, 5 mL of 20-40 mesh particles were weighed and added to the middle of the reactor, and the ends of the reaction tube were filled with quartz sand. The reaction temperature was 650 °C, nitrogen pressure was 1.0 MPa, and volumetric space velocity was 0.5 h^{-1}. After allowing the reaction system to stabilize for 3 h, the product in the product tank was emptied. Following the continuous operation, the sample was evaluated online using an Agilent GC 7890 gas chromatograph.

Evaluation Indicators and Calculation Methods

The conversion rate (X) of the catalytic cracking of n-hexane was evaluated using the mass ratio of n-hexane which was involved in the reaction. The masses of ethylene and propylene which were obtained by cracking were represented by $W_{CiHj,\ t}$, and the total mass of the products which was obtained by cracking was represented by $W_{product}$. Furthermore, the mass of n-hexane consumed by the reaction was represented by $W_{n\text{-}C6H14,\ t}$, whereas the initial amount of n-hexane in the device was represented by $W_{n\text{-}C6H14,\ o}$. The total selectivity for ethylene and propylene was represented by S_{CiHj}, and the yield was represented by Y_{CiHj}. The expressions used to calculate the conversion rate, selectivity, and yield are given below:

$$X = \frac{W_{n-C_6H_{14},o} - W_{n-C_6H_{14},t}}{W_{n-C_6H_{14},o}} \times 100\% \tag{1}$$

$$S_{C_iH_j} = \frac{W_{C_iH_j,t}}{W_{\text{product}}} \times 100\% \tag{2}$$

$$Y_{C_iH_j} = X \cdot S_{C_iH_j} \times 100\% \tag{3}$$

RESULTS AND DISCUSSION

Catalytic Cracking of n-hexane over Synthetic ZSM-5

As shown in Table 2, HZ-170-48h-11 exhibited the best conversion of n-hexane and maximum selectivity and yield of ethylene and propylene. Sheng-tao QU, Dong-mei LIU, Xin SHI, Hai-yan WANG, and Xin WANG, Effects of ZSM-5 Preparation Conditions on Textural Properties and Catalytic Cracking of n-Hexane, Table 2

The conversion rate was 91%, and the total selectivity and yield of ethylene and propylene were 60% and 54.6% respectively (calculated according to Equations 1 to 3. HZ-130-12h-11 exhibited the worst conversion rate (only 32%), and HZ-130-48h-11.5 showed the worst selectivity and yield (12% and 4.0%, respectively). From K_1, K_2, K_3, and K_4 [14, 15], the optimal synthesis condition was calculated as $A_3B_3C_1$ (HZ-170-48h-11 catalyst). According to the actual cracking reaction results, the optimum condition for the catalytic cracking of n-hexane was also $A_3B_3C_1$. To further analyze the influence of various factors on the catalytic cracking performance of the catalyst, the ANOVA was performed on the conversion of n-hexane, the selectivity, and yield of ethylene and propylene. It can be seen from Table 3 that the crystallization temperature, crystallization time, and pH value do not exceed the value of $F_{0.01}$, and the significant order of the three factors on the catalytic cracking effect is crystallization temperature > crystallization time > pH value.

Table 2: Results of catalytic cracking of n-hexane over ZSM-5 zeolites synthesized under different conditions (Sheng-tao QU, Dong-mei LIU, Xin SHI, Hai-yan WANG, and Xin WANG, Effects of ZSM-5 Preparation Conditions on Textural Properties and Catalytic Cracking of n-Hexane).

Sample	X (%)	S (%)	Y (%)
HZ-130-12h-11	32	13	4.2
HZ-130-24h-12.5	35	17	6.0
HZ-130-48h-11.5	33	12	4.0
HZ-130-72h-12	36	14	5.0
HZ-150-12h-12.5	39	19	7.4
HZ-150-24h-11	57	36	20.5
HZ-150-48h-12	73	48	35.0
HZ-150-72h-11.5	80	53	42.4
HZ-170-12h-11.5	42	22	9.2
HZ-170-24h-12	87	56	48.7
HZ-170-48h-11	91	60	54.6
HZ-170-72h-12.5	94	56	52.6
HZ-190-12h-12	42	25	10.5
HZ-190-24h-11.5	63	40	25.2
HZ-190-48h-12.5	76	50	38.0
HZ-190-72h-11	68	44	29.9
K_1	136 56 19.2	155 79 31.3	248 153 109.2
K_2	249 146 105.3	242 149 100.4	218 127 80.8
K_3	314 194 165.1	273 170 131.6	238 143 99.2
K_4	249 159 103.6	278 167 129.9	244 142 104.0
R (Range)	178 138 145.9	123 91 100.3	30 26 28.4

Note: K_i is the sum of the experimental data corresponding to the "i" level of the three columns of crystallization temperature, crystallization time, and pH (ΣX || ΣS || ΣY); X is the conversion rate of n-hexane; S and Y are the selectivity and yield, respectively, of ethylene and propylene.

Table 3: Variance analysis table of test results (Sheng-tao QU, Dong-mei LIU, Xin SHI, Hai-yan WANG, and Xin WANG, Effects of ZSM-5 Preparation Conditions on Textural Properties and Catalytic Cracking of n-Hexane).

Performance	Source	SS	df	MS	F	Threshold	Significance
X (%)	A	4104.500	3	1368.167	9.350	$F_{0.01}(3,6)=9.78$ $F_{0.05}(3,6)=4.76$ $F_{0.1}(3,6)=3.29$	***
	B	2431.500	3	810.500	5.539		**
	C	133.000	3	44.333	.303		*
	Error	878.000	6	146.333			
	Total	63716.000	16				
S (%)	A	2645.687	3	881.896	9.702		***
	B	1356.187	3	452.062	4.973		**
	C	86.188	3	28.729	.316		*
	Error	545.375	6	90.896			
	Total	24585.000	16				
Y (%)	A	2699.035	3	899.678	7.167		***
	B	1650.215	3	550.072	4.382		**
	C	114.590	3	38.197	.304		*
	Error	753.230	6	125.538			
	Total	14879.960	16				

Characterization of ZSM-5 Samples

X-Ray Diffraction (XRD) Analysis

In Figure 1, the XRD patterns of ZSM-5 zeolites synthesized under various conditions are shown, and the corresponding relative crystallinities are listed in Table 4.

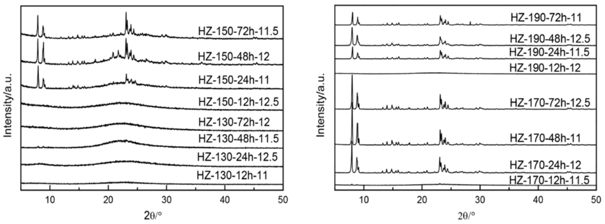

Figure 1: XRD patterns of ZSM-5 catalysts prepared under various conditions (Sheng-tao QU, Dong-mei LIU, Xin SHI, Hai-yan WANG, and Xin WANG, Effects of ZSM-5 Preparation Conditions on Textural Properties and Catalytic Cracking of n-Hexane).

Table 4: Relative crystallinities of ZSM-5 zeolites synthesized under various preparation conditions (Sheng-tao QU, Dong-mei LIU, Xin SHI, Hai-yan WANG, and Xin WANG, Effects of ZSM-5 Preparation Conditions on Textural Properties and Catalytic Cracking of n-Hexane).

Sample	Relative crystallinity (%)	Sample	Relative crystallinity (%)
HZ-130-12h-11	6	HZ-170-12h-11.5	23
HZ-130-24h-12.5	22	HZ-170-24h-12	78
HZ-130-48h-11.5	14	HZ-170-48h-11	98
HZ-130-72h-12	17	HZ-170-72h-12.5	82
HZ-150-12h-12.5	28	HZ-190-12h-12	25
HZ-150-24h-11	63	HZ-190-24h-11.5	68
HZ-150-48h-12	75	HZ-190-48h-12.5	77
HZ-150-72h-11.5	72	HZ-190-72h-11	72

When the crystallization times were 24, 48, and 72 h at pH 11, 11.5, 12, and 12.5, and crystallization temperatures were 150, 170, and 190 °C, diffraction peaks were observed at 2θ = 7.90°, 9.05°, 23.99°, 24.55°, and 25.85°, which were characteristics of ZSM-5. Thus, the catalysts synthesized under these conditions are all ZSM-5. However, the samples obtained at crystallization times of 24, 48, and 72 h, pH of 11, 11.5, 12, and 12.5, and crystallization temperature of 130 °C were almost amorphous. This finding indicated that ZSM-5 cannot be synthesized under these experimental conditions because the autogenous pressure in the autoclave caused by the crystallization temperature is too low, which the conditions are not conducive to the formation of the MFI skeleton structure [16]. As shown in Table 2, the total conversion rate of n-hexane is only 32% for HZ-130-12h-11, and the selectivity and yield of ethylene and propylene are both low, indicating that the synthesized amorphous substance is not suitable for the cracking reaction of n-hexane.

When (1) the crystallization temperature was increased to 150 °C, and (2) the crystallization time was 12 h, the XRD pattern of the product only exhibited one peak, which the peak indicates that the catalyst was still in the growth phase. As the crystallization time gradually increased, the characteristic peaks of ZSM-5 became stronger and then weakened, and a heterogeneous peak appeared at 2θ = 20.56°. Moreover, this observation indicated that the catalyst synthesized at this crystallization temperature contained heterocrystals, which may be due to the formation of other zeolites. At this crystallization temperature, the catalyst with the highest relative crystallinity was HZ-150-48h-12, and its total conversion rate was 73%; the selectivity and yield of ethylene and propylene were 48% and 35.0%, respectively. When the crystallization temperature was 190 °C, the relative crystallinity of the zeolites decreased. At a crystallization time of 72 h, the characteristic peak of the quartz phase appeared at 2θ = 27.90°. Moreover, this result showed that a significantly high crystallization temperature can also be problematic. That is, an excessive crystallization temperature can cause deformation or partial destruction of the micelles formed by the surfactant molecules of the templating agent, thereby lowering the order of the pore structure in the product. Furthermore, ZSM-5 tends to transform into other crystal phases at high temperatures.

As shown in Table 4, the relative crystallinity of the zeolites first increases and then decreases as the crystallization time increases, indicating an optimal crystallization time for the synthesis of ZSM-5 can be obtained under the examined experimental conditions. Longer crystallization times will increase the agglomeration of crystal nuclei in the mixture, cause more Si atoms to enter the surface of the catalyst, and allow the skeleton to form heterocrystals, thus affecting the crystallinity of the synthetic catalyst. According to Tables 2 and 3, when the crystallization temperatures were 150, 170, or 190 °C, higher relative crystallinities of the catalyst corresponded to higher selectivities for ethylene and propylene.

When the crystallization temperature was 170 °C, the crystallization time was 48 h, and liquor pH was 11, and the XRD pattern of the synthetic catalyst (HZ-170-48h-11) was relatively flat (Figure 1). The relative crystallinity of this catalyst was the highest (98%, Table 4), indicating that there were fewer amorphous crystals.

When this catalyst was applied to the reaction, the total conversion of n-hexane was the highest (91%) and the selectivity and yield of ethylene and propylene were also higher (60% and 54.6% respectively). Based on the above analysis, four ZSM-5 catalysts with the best and worst conversion rates, selectivities, and yields (HZ-150-24h-11, HZ-150-48h-12, HZ-170-48h-11, and HZ-170-72h-12.5) were chosen for further characterization. Finally, the effects of the textural properties of the synthesized ZSM-5 on the catalytic cracking reaction performance were studied.

BET Analysis

In Table 5, the specific surface areas and pore volumes of the selected ZSM-5 zeolites are shown.

Table 5: Pore structure properties of ZSM-5 zeolites synthesized under various conditions (Sheng-tao QU, Dong-mei LIU, Xin SHI, Hai-yan WANG, and Xin WANG, Effects of ZSM-5 Preparation Conditions on Textural Properties and Catalytic Cracking of n-Hexane).

Sample	S(Total) ($m^2 \cdot g^{-1}$)	S(Micropore) ($m^2 \cdot g^{-1}$)	V_p(Total) ($cm^3 \cdot g^{-1}$)	V_p(Micropore) ($cm^3 \cdot g^{-1}$)
HZ-150-24h-11	185.7	172.9	0.11	0.10
HZ-150-48h-12	287.5	268.1	0.14	0.11
HZ-170-48h-11	498.8	485.6	0.20	0.18
HZ-170-72h-12.5	427.3	412.1	0.18	0.15

When the crystallization temperature was increased from 150 to 170 °C, and the crystallization time was extended from 24 to 48 h at the pH value = 11, the total area and total pore volume were increased. This observation indicated that under these experimental conditions, the polymerization degree of the silicate ions in the liquor is ideal, and ZSM-5 with good crystallinity can be formed. As the crystallization temperature increased, the crystallization time lengthened, and the crystal structure of the zeolite in the reactor also increased. When the crystallization temperature reached 170 °C (48 h), the crystals grew further. Therefore, the total area and total pore volume of the synthetic catalyst reached the maximum values of 498.8 m^2g^{-1} and 0.20 cm^3g^{-1} respectively. Furthermore, the micropore specific surface area and volume reached 485.6 m^2 g^{-1} and 0.18 cm^3 g^{-1} respectively. As the cracking reaction of n-hexane mainly results from the interaction of the positive carbon ions through the pentacoordinate intermediate mechanism, a larger surface area and pore volume can be attributed to the exposure of more active centers on the catalyst. As a result, n-hexane can interact with more positive carbon ions, and the conversion rate of n-hexane will increase. When the area of the catalyst is larger, the probability of n-hexane encountering an exposed active center on the catalyst is increased, and the conversion rate will be higher. Moreover, the larger pore volume contributes to the diffusion of reactants and products, making the catalyst less resistant to carbon deposition. Therefore, the activity and n-hexane conversion rate of the catalyst synthesized under these conditions are the highest. When the crystallization time exceeded 48 h, the total area and pore volume decreased. When the crystallization time was too long, the grain size of the synthesized catalyst became larger, and thus the pore volume was reduced [17].

NH_3-TPD Analysis

In Figure 2, the NH_3-TPD curves of the selected ZSM-5 catalysts are shown.

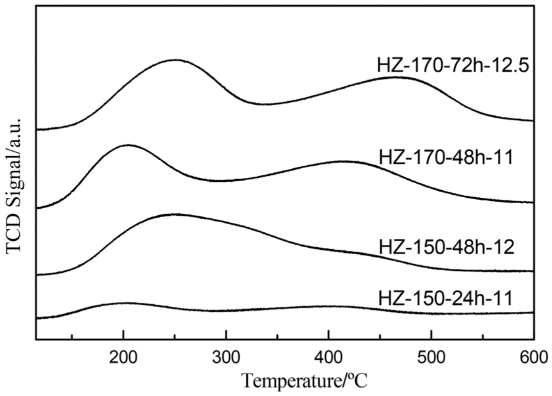

Figure 2: NH3-TPD curves of ZSM-5 zeolites synthesized under various conditions (Sheng-tao QU, Dong-mei LIU, Xin SHI, Hai-yan WANG, and Xin WANG, Effects of ZSM-5 Preparation Conditions on Textural Properties and Catalytic Cracking of n-Hexane).

The desorption peaks which are observed near 200 and 400 °C correspond to the weak/medium acid and strong acid centers of the zeolite respectively. The two desorption peaks of HZ-150-24h-11 are small, indicating that this catalyst has few strong acids and weak acid sites. As the crystallization temperature and the crystallization time are not optimal, the crystals cannot not fully grow; therefore, the amount of Al on the skeleton and the acidity of the catalyst were lower [18]. HZ-150-48h-12 shows a distinct weak acid desorption peak between 200 and 350 °C, whereas the strong acid desorption peak near 400 °C is small, indicating that the amount of strong acid sites is low.

The catalytic cracking reaction of alkanes is the result of the interaction of the five-coordinate intermediate mechanism and the positive carbon ion mechanism [19]. In general, short-chain n-alkanes are dominated by the five-coordinate intermediate mechanism [20]. In the cracking reaction of n-hexane, short-chain normal paraffin, the first step of the reaction is the formation of a pentacoordinate intermediate, and the process requires a certain intensity of H+. As this process is slow, it is the rate-controlling step. Therefore, increasing the acid strength and the volume of acid sites will contribute to the progress of this step. In comparison with the small amount of medium/strong acid and weak acid sites in HZ-150-24h-11, the content of weak/medium acid sites was higher in HZ-150-48h-12, but the content of strong acid sites was lower. Therefore, the application of these two catalysts to the n-hexane cracking reaction did not result in high cracking conversion rates.

As shown in Figure 2, HZ-170-48h-11 exhibits two distinct desorption peaks near 200 and 400 °C. This observation indicates that when the crystallization temperature was 170 °C, the crystallization time was 48 h, and the pH was 11, the ZSM-5 zeolite had grown sufficiently and contained a large amount of weak/medium acid and strong acid sites. Application of this catalyst to the n-hexane cracking reaction resulted in a remarkably increased cracking conversion rate. The peak areas of the weak/medium acid and strong acid sites in HZ-170-72h-12.5 were increased compared with those of HZ-170-48h-11. This increase is due to prolonged crystallization time and increased pH. The amounts of Si and Al in the skeleton of the zeolite increased, but the amount of Al in the skeleton increased faster than the amount of Si [21,22]; therefore, both the weak acid and strong acid sites in HZ-170-72h-12.5 increased. When this catalyst was applied to the cracking reaction of n-hexane, the conversion rate increased further to 94%, but the selectivity and yield of ethylene and propylene decreased to 56% and 52.6% respectively. This behavior may be due to the fact that the acid strength and the volume of acid sites were too high, thereby increasing the content of by-products such as light alkanes and aromatics [23,24], which decreases the selectivity and yield of ethylene and propylene. This analysis reveals that the acid strength and acid amount of HZ-170-48h-11 were optimal for the catalytic cracking reaction of n-hexane.

Py-IR Analysis

In Figure 3, the Py-IR spectra of the four selected catalysts are shown.

In the spectra, the adsorption peaks at 1544 and 1450 cm^{-1} correspond to Brønsted (B) acid sites and Lewis (L) acid sites respectively.

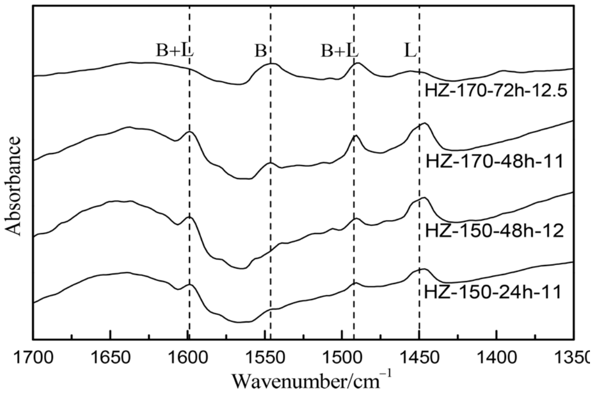

Figure 3: Py-IR spectra of ZSM-5 zeolites synthesized under various conditions
(Sheng-tao QU, Dong-mei LIU, Xin SHI, Hai-yan WANG, and Xin WANG, Effects of ZSM-5 Preparation Conditions on Textural Properties and Catalytic Cracking of n-Hexane).

Moreover, two adsorption peaks assigned to both B and L acid sites appear near 1490 and 1598 cm^{-1}. Both HZ-150-24h-11 and HZ-150-48h-12 exhibited obvious L acid peaks, while no B acid peaks were evident. This observation indicates that HZ-150-24h-11 and HZ-150-48h-12 contain more L acid sites than B acid sites. As B acid sites play a major role in the positive carbon ion reaction [24], the conversion of n-hexane over these two catalysts was not high. With the increase in the crystallization temperature, HZ-170-48h-11 and HZ-170-72h-12.5 showed obvious B acid peaks at 1544 cm^{-1}. The area of the B acid peak of HZ-170-72h-12.5 was larger than that of HZ-170-48h-11, indicating that the content of B acid sites in HZ-170-72h-12.5 was greater. The acidity of the zeolite with more B acid sites can accelerate the cracking reaction of n-hexane, but the rate of side reactions related to strong acid sites will also increase. Thus, the conversion of n-hexane increased over the HZ-170-72h-12.5 catalyst, but the selectivity and yield of the desired products decreased, which is consistent with the NH_3-TPD results.

Scanning Electron Microscopy (SEM) Analysis

In Figure 4, SEM images of the four selected catalysts are shown.

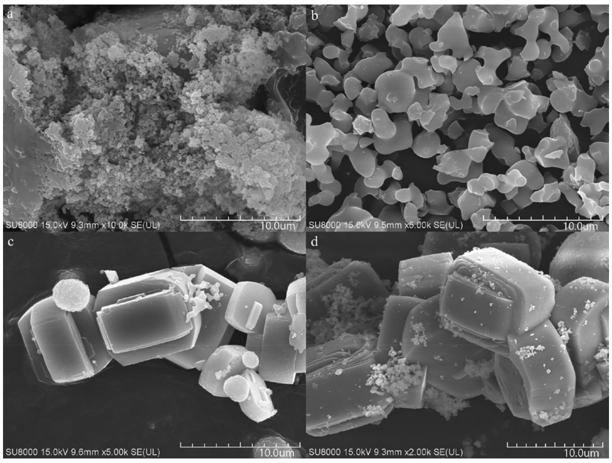

Figure 4: SEM images (scale bars: 10 μm) of ZSM-5 zeolites synthesized under various conditions: (a) HZ-150-24h-11, (b) HZ-150-48h-12, (c) HZ-170-48h-11, and (d) HZ-170-72h-12.5 (Sheng-tao QU, Dong-mei LIU, Xin SHI, Hai-yan WANG, and Xin WANG, Effects of ZSM-5 Preparation Conditions on Textural Properties and Catalytic Cracking of n-Hexane).

The morphology of HZ-150-24h-11 consists of small particles without fixed shapes, indicating that under these conditions, the zeolite is in the growth phase and has not yet fully grown. Therefore, this sample has low crystallinity and a small surface area and is not suitable for the n-hexane cracking reaction. Prolonging the crystallization time and increasing the pH caused the crystal grains in HZ-150-48h-12 to grow, with the sample mainly composed of massive spherical particles of various sizes. This observation indicated that the zeolite was still in the growth phase under these conditions. However, which also increased the skeletal density, the grain size, the area, and the pore volume of this catalyst in comparison with HZ-150-24h-11. Thus, the conversion in the cracking reaction increased to 73%, but it was still not high. With an increase in the crystallization temperature to 170 °C, HZ-170-48h-11 exhibits obvious particles with smooth surfaces. This morphology indicated that ZSM-5 zeolite particles have been grown, and the maximum surface area and total pore volume are obtained for this catalyst. Further extending the crystallization time and increasing the pH of the mother liquor led to a decrease in the surface area and total pore volume in HZ-170-72h-12.5. As shown in Figure 4, HZ-170-72h-12.5 has a similar morphology to HZ-170-48h-11, but many heterocrystals are observed on the surfaces of the particles. In the reaction, although the hexane cracking conversion rate over HZ-170-72h-12.5 is higher than that over HZ-170-48h-11, the selectivity and yield of the target products are lower.

Performance Evaluation

In Figure 5, the results of online evaluation of the conversion of n-hexane over the four selected catalysts are shown. The online evaluation was started after the temperature and pressure of the cracking reaction system were stable for 3 h.

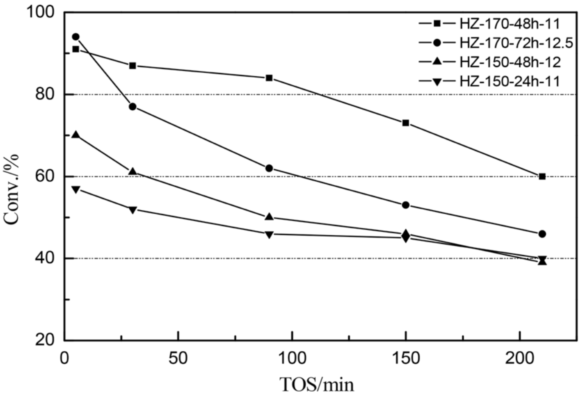

Figure 5: Online evaluation (TOS) of catalytic cracking conversion of n-hexane over the four selected catalysts. (Sheng-tao QU, Dong-mei LIU, Xin SHI, Hai-yan WANG, and Xin WANG, Effects of ZSM-5 Preparation Conditions on Textural Properties and Catalytic Cracking of n-Hexane).

The total conversions observed for HZ-150-24h-11 and HZ-150-48h-12 were low, mainly because the crystallization temperature of 150 °C did not allow the full growth of the skeleton structure or the internal structure; therefore, these catalysts were not suitable.

The initial conversion rate of HZ-170-72h-12.5 was 94%, but after 0.5 h of continuous reaction, the conversion rate rapidly decreased to 77%. As the reaction time increased, the total conversion rate decreased further, with a total conversion rate of only 46% at a reaction time of 210 min. This decrease was mainly caused by the acid centers containing a large amount of B acid sites, as shown in Figures 2 and 3. If the content of B acid sites is high, the volume of aromatic hydrocarbons and carbon deposits will increase, and excessive carbon deposition will cause faster deactivation of the catalyst [22]. In addition, the pH of the mother liquor was too high during the synthesis of HZ-170-72h-12.5. The higher pH caused a lower polymerization degree of silicate ions in the pore walls, thus lowering the thermal stability and hydrothermal stability of the catalyst. Therefore, the stability of HZ-170-72h-12.5 was poor, and the catalyst was deactivated faster.

The initial conversion rate of HZ-170-48h-11 was 91%. As the reaction time increased to 100 min, the conversion rate of n-hexane decreased slowly. However, at longer reaction times, the conversion rate decreased rapidly, and the total conversion rate was only 60% at a reaction time of 210 min. The stability of HZ-170-48h-11 was better than that of HZ-170-72h-12.5, mainly because the crystallization time and pH were more suitable. The surface area, total pore volume, and acidity of this optimal catalyst (HZ-170-48h-11) were moderate, with high thermal stability and hydrothermal stability. The final deactivation of HZ-170-48h-11 was mainly due to the polymerization of n-hexane under the action of positive carbon ions, as the resulting macromolecular compound covers the active centers on the surface of the zeolite.

CONCLUSIONS

According to this study, the following results have been obtained:

(1) The primary and secondary relationships among the three preparation conditions were analyzed by the orthogonal test method. The effects of the preparation conditions on ZSM-5 synthesis decreased in the following order: crystallization temperature > crystallization time > pH. When the synthetic catalysts were applied to the cracking reaction of n-hexane, HZ-170-48h-11 exhibited high n-hexane conversion rate, high ethylene and propylene selectivity (60%), and a high ethylene and propylene yield (54.6%). Thus, these findings will provide insights into the selection and preparation of catalysts for the cracking of short-chain alkanes.

(2) At crystallization temperatures of 150 °C or lower, the catalyst was not fully grown, even if the crystallization time was extended. When the crystallization temperature was increased to 170 °C, a fully grown ZSM-5 zeolite was obtained with a crystallization time of 48 h at pH 11. Further extending the crystallization time and increasing the pH increased the acidity of the catalyst, but also contributed to the growth of heterocrystals. When the crystallization temperature was 190 °C, the heterogeneous peak of the quartz phase (SiO_2) increased, which affected the crystallinity of ZSM-5.

(3) Finally, the catalytic stability evaluation

revealed that the initial activity of HZ-170-72h-12.5 was the highest, but this catalyst was unstable. Although the initial activity of HZ-170-48h-11 was lower than that of HZ-170-72h-12.5, the stability of this catalyst was better. Thus, the conditions of 170 °C, 48 h, and pH value = 11 were optimal for synthesizing a ZSM-5 catalyst, which the optimal conditions were suitable for the catalytic cracking of n-hexane.

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NOMENCLATURES

DCC	: Deep catalytic cracking
X	: conversion rate of n-hexane, %
S	: total selectivity of ethylene and propylene, %
Y	: total yield of ethylene and propylene, %
$W_{CiHj, t}$	: the mass of ethylene and propylene obtained by cracking, g
$W_{product}$	: total mass of products obtained by cracking, g
$W_{n\text{-}C6H14, t}$	: the mass of n-hexane consumed during cracking,g
$W_{n\text{-}C6H14, o}$	: the initial amount of n-hexane, g
K_i	: the sum of the experimental data corresponding to the “i” level of the crystallization temperature, Crystallization time, and pH value.

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