

Article

Protolytic Ring-Opening Cracking of Methylcyclohexane over Hierarchical High-Silica USY Zeolite: A Haag-Dessau Cracking

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Abstract: To reveal the influence of acid sites with different spatial locations of USY zeolite with different micro-/mesoporous structures and Si/Al ratio, catalytic cracking of methylcyclohexane on the zeolites is employed to study the synergism effects of acid sites and porous structures (“active region”) in the hierarchical USY zeolites. The results showed that the hierarchical USY zeolites have increased numbers of accessibly strong Brønsted acid sites and greatly enhanced diffusion ability due to the hierarchical pore-structure, resulting in mainly monomolecular protolytic scission in cracking reactions and less bimolecular hydrogen transfer. The isomerization reaction is from intramolecular transalkylation and the isomerics are the intermediates of the cracking reaction. The protolytic cracking that occurs in hierarchical high-silica USY-zeolites follows the Haag-Dessau cracking.

Keywords: protolytic cracking; USY zeolite; hierarchical structure; ring-opening cracking; strong Brønsted acidity



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1. Introduction

Fluid catalytic cracking (FCC) is a process for the conversion of straight-run gas oils, vacuum gas oils, and heavy stocks into light fuel oil. The hydrocarbon types present in the FCC feed are a complex mixture that usually includes 10–30 wt% cyclic. The main acid active components of the FCC catalyst are zeolites with different topological structures. Zeolites are microporous crystalline aluminosilicates with a high surface area, well-defined pore size and structure from the particular topological framework, as well as an adjustable acidity by the presence of Al inside the framework. However, diffusion limitation, especially during the process of bulky molecules caused by their similarity between the size of the involved molecular species and the diameter of micropore channels, severely hinders their practical application. This hindrance is a factor because mass transfer always plays an important role in the industrial processes in which zeolites are involved.

The intracrystalline diffusivity of molecular species involved in these processes is often the rate-limiting factor in the whole kinetics of the processes. Given this situation, how to overcome the diffusion limitation of zeolite has been a major issue in enhancing the accessibility and availability of active sites within the zeolite and further improving the catalytic performance of the zeolite [1–3]. It is well-known that introducing mesopores into conventional microporous zeolites to form mesoporous materials is an effective solution to eliminate the diffusion limitation of micropores in zeolites. The hierarchical pores in conventional microporous zeolite can be created by a template approach or post-treatment. The presence of mesopores in zeolite catalysts can enhance the mass transport of reactive molecules due to their shorter average diffusion path length, which significantly improves both catalytic activity and the lifetime of zeolite catalysts. The positive effect of mesopores on zeolites has been proven in a number of industrial processes where zeolite catalysts

are used [2,4–8]. Jiao et al. [9] studied the acetalization reaction of cyclohexanone with pentaerythritol in hierarchically structured Y-zeolite, discovering that the introduction of mesopores leads to a much better performance than the conventional Y-zeolite, which could be attributed to the enhanced diffusion ability of large-sized guest molecules through the combination of meso- and microstructures. García et al. [10] explored the catalytic cracking of bio-oils in a mesoporous Y-zeolite created by desilication, finding that the desilicated zeolite is more effective than the parent zeolite to deoxygenate bio-oil and produces more hydrocarbons, with higher selectivity to olefins and lower selectivity to aromatics, which is a result of the improvements in the diffusion of bulky molecules in bio-oils, such as phenolic ethers.

Y-zeolites consist of sodalite cages 1.3 nm in diameter interconnected via hexagonal prisms of 0.74 nm diameter (12-membered rings). Due to the unique micropore structure and the variable framework composition (Si/Al ratio) by the application of post-synthetic dealumination modifications, such as ultrastable Y (USY), it has become the most important zeolitic catalyst with remarkable activity, selectivity and hydrothermal stability in numerous petrochemical industries, such as fluid catalytic cracking (FCC) and hydrocracking, which are widely used in the oil-refining and petrochemical industry [11–13]. Besides increasing Si/Al ratios, the dealumination of the framework can also lead to the introduction of a secondary network of mesopores in the zeolite crystal. It is generally accepted that the widespread use of modified USY zeolites is based on two main features: an adjustable acidity and improved molecular transfer ability generated by dealumination. The modification of zeolite inevitably results in changes in pore structure and acidity, which will exert an important influence on the catalytic performance [14,15].

In the FCC and hydrocracking processes, the cracking activity can be attributed to the Brønsted acidity of zeolite [16,17]. In addition, naphthenes are important constituents of FCC feedstocks [18,19]. According to the literature, the transformations of alkanes and aromatics have been studied extensively, but relatively fewer studies have been devoted to naphthene's transformation on the zeolite catalysts [20–24]. However, the transformation, such as the methylcyclohexane (MCH) transformation, involves all of the reactions occurring during VGO conversion, including isomerization, cracking, and aromatization by hydrogen transfer and coking.

Although the methylcyclohexane transformation is complex, it can be used as a model reaction to evaluate catalyst performance and to characterize both the acidity and porosity of zeolites [24]. Therefore, in the present work, MCH is used as a model molecular of naphthene, and its conversion behaviors on three types of zeolite Y-catalysts with different Si/Al ratios and porosities are studied to establish the relation of MCH conversion and catalyst properties for a better understanding of these reactions and to reveal the influence of acid sites with different spatial locations of the USY zeolite with different micro-/mesoporous structure and Si/Al ratio, a synergism effect of acid site and porous structure ("active region") in the hierarchical USY zeolites. This work is conducive to the design and preparation of an industrial hydrocracking catalyst of heavy oil with cycloparaffin hydrocarbons.

2. Results and Discussion

2.1. Structure, Porosity and Morphology

The XRD patterns of the three Y-zeolite samples and their corresponding relative crystallinities are displayed in Figure 1a and Table 1, respectively. It can be seen from the XRD patterns that, similar to the unmodified parent CPY zeolite, modified FUSY and RUSY zeolite samples exhibit exactly the same characteristic diffraction peaks corresponding to FAU topology, confirming the preservation of the framework structure of Y zeolite. Pore structures of the three Y-zeolite samples are analyzed by using N₂ adsorption/desorption isotherms at 77 K, as depicted in Figure 1b. Unlike CPY exhibiting a type I isotherm for typical microporous materials according to the IUPAC classification, FUSY and RUSY zeolites show a combination of type I and type IV isotherms. In addition to the micro-

pore adsorption at low relative pressures, the isotherms contain mesopore filling with a distinctive hysteresis loop at higher relative pressures of above 0.4, which reflect the preservation of their microporous structures and the presence of additional mesoporosity and macroporosity within the FUSY and RUSY zeolites. From the pore structure parameters listed in Table 1 derived from the isotherm data, the total surface areas (S_{BET}) of FUSY and RUSY zeolites show a significant decline compared with those of CPY, but the micropore volume (V_{mic}) changes are as significant. These results indicate that the introduction of mesopores and macropores by post-synthesis has no obvious effect on the microporous structure of the first two samples. Their mesopore volumes are larger than the latter due to the presence of mesoporous structure in the samples.

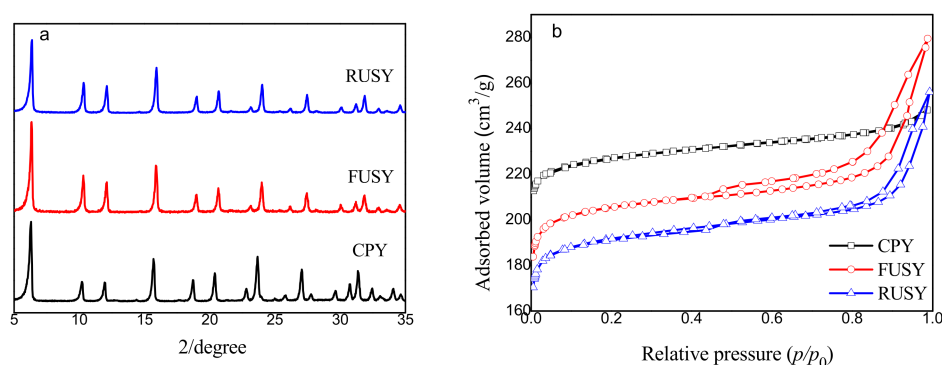


Figure 1. XRD patterns (a) and nitrogen adsorption/desorption isotherms (b) of the three Y-zeolite samples.

Table 1. Pore structure parameters and compositions of the three Y-zeolite samples.

Samples	S_{BET} (m^2/g)	V_{mic} (cm^3/g)	V_{meso} (cm^3/g)	RC ^a (%)	$n_{\text{Si}}/n_{\text{AlF}}$ ^b	$n_{\text{Si}}/n_{\text{Albulk}}$ ^c
CPY	933	0.33	0.08	100	2.6	2.4
FUSY	756	0.28	0.13	70	5.5	4.6
RUSY	776	0.27	0.11	69	13.3	10.5

^a Relative crystallinity; ^b Calculated by XRD; ^c Calculated by XRF.

The SEM images of the three samples are displayed in Figure 2 to shed light on the difference in the morphology for microporous CPY and mesoporous FUSY and RUSY zeolite samples. As shown in the SEM images, there are no morphologic changes in the zeolite crystals, despite the drastic changes in pore architecture upon modification. However, the occurrence of intracrystalline mesopores and the increase of surface roughness are obvious for both FUSY and RUSY samples. Moreover, much more mesopores are observed in FUSY than RUSY.

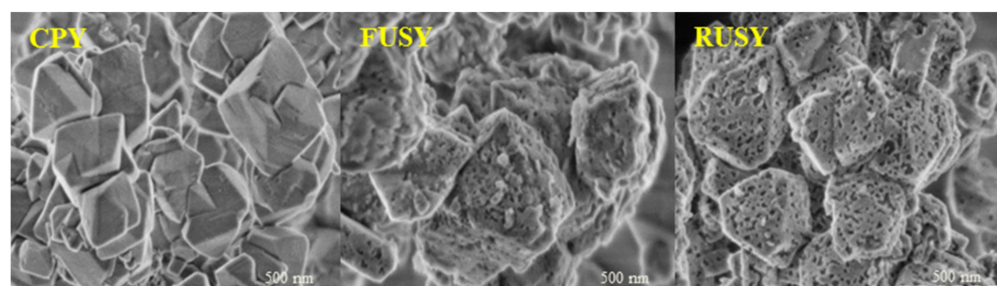


Figure 2. SEM images of three Y-zeolite samples.

In addition, the global (Si/Al bulk) and framework Si/Al ratios (Si/Al_F) of the three Y-samples were determined by X-ray fluorescent (XRF) and XRD, respectively. From Table 1, it can be seen that both global and framework Si/Al ratios of the FUSY and RUSY samples are higher than that of the CPY sample due to the dealumination (desilicoaluminate) in the process of modification.

2.2. Acidity

Pyridine-adsorbed FTIR spectroscopy in the 1600–1400 cm^{−1} region was employed to characterize the acid properties of the three Y-zeolite samples. There are three sharp bands due to N–H stretching vibrations of pyridine in this region. The strong band at 1490 cm^{−1} is due to the pyridine adsorbed on both Brønsted and Lewis acid sites (BAS and LAS), while bands at 1540 cm^{−1} and 1450 cm^{−1} are due to the protonation of pyridine molecule by BAS and pyridine adsorbed on LAS, respectively. The amounts of BAS and LAS were calculated by using the values of the molar extinction coefficients of these bands, 1.13 and 1.28 cm mmol^{−1}, respectively [25], as shown in Table 2. The data displays that the numbers of LAS, BAS and total acid sites of the modified Y-zeolites decrease, along with the increase of the molar ratio of Si/Al after modification, which can be assumed that the Al content determines the amount of the acidity sites. However, compared with the unmodified CPY, the relative amounts of medium-strong and strong acid sites of FUSY and RUSY increase obviously, which correspond to the chemisorbed pyridine at 523 K and 623 K, respectively. Of interest is that the numbers of strong BAS in FUSY and RUSY samples surpass CPY, exhibiting the order of FUSY (225 μmol/g) > RUSY (200 μmol/g) > CPY (193 μmol/g). It is important to note that these strong Brønsted acid sites are accessible by MCH because of their similar molecular size to pyridine. The changes in acidity arise from the extraction of the framework aluminum and minor silicon upon modification, resulting in the formation of meso(macro)pores and increases in the bulk and framework Si/Al ratios.

Table 2. Pyridine FTIR data on the three Y-zeolite samples.

Sample	T (K)	BAS (μmol/g)	LAS (μmol/g)	Total (μmol/g)
CPY	423	322	298	620
	523	292	194	486
	623	193	171	364
FUSY	423	287	76	363
	523	269	57	327
	623	225	46	271
RUSY	423	246	65	311
	523	231	50	282
	623	200	38	239

2.3. Diffusion Evaluation

In the present work, methylcyclohexane as a probe molecule, the diffusion properties of three Y-zeolites are evaluated by using the ZLC technique to study the effects of additional meso(macro)pore and the acidity in zeolite on the molecular diffusion. Figure 3 displays the representative experimental and theoretical ZLC response curves for methylcyclohexane desorption in three Y-zeolite samples at 373 K. As is shown, the good agreement between the experimental results (symbols) and theoretical fittings (solid lines) is clearly observed for three samples, which confirms the validity of the applied theoretical model. The experimental results show that mesoporous FUSY and RUSY present a much higher desorption rate than microporous CPY under the same condition, while only a slightly higher desorption rate over RUSY than that of FUSY is observed. Further, the effective diffusion time constants D_{eff}/R^2 from the desorption kinetics curves at 333 K, 353 K and 373 K are displayed in Figure 4, showing that the methylcyclohexane molecule possesses much higher D_{eff}/R^2 values on the modified FUSY and RUSY than on the CPY; that is, the

values increase in the order of CPY << FUSY < RUSY. These phenomena reflect the greatly enhanced molecular transport in FUSY and RUSY zeolite samples.

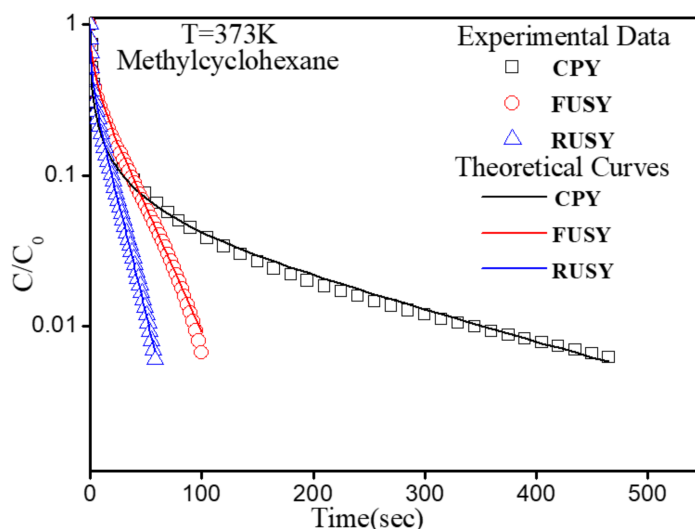


Figure 3. ZLC desorption curves at 373 K for methylcyclohexane on the three Y-zeolite samples.

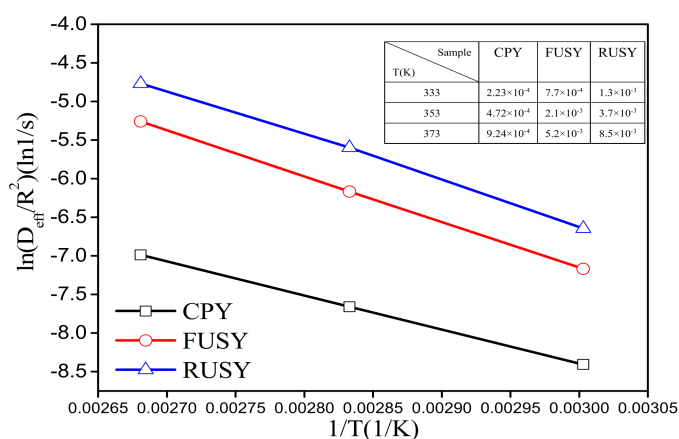


Figure 4. The relationship between the effective diffusion time constant and temperature at 333 K, 353 K, and 373 K for methylcyclohexane (MCH) on the three Y-zeolite samples.

On the basis of previous research [26–28], it is known that the diffusion (transfer ability) for a given hydrocarbon inside zeolite is strongly dependent on the pore structure and surface acidity. The existence of mesopores and lower acidic site density inside zeolite are beneficial to the diffusivity of molecules. The much lower diffusion rate over CPY compared to FUSY and RUSY is just because of the remarkable diffusion limitation created by inherent microporous structures and the stronger molecule-zeolite interaction resulting from more acid sites restricting the molecular transport, whereas because of the introduction of secondary meso(macro)pores and the increasing of Si/Al ratio for FUSY and RUSY, the resistance of molecule transport is reduced, and the diffusion ability is increased. Moreover, in comparison with RUSY, though the mesoporosity of FUSY is higher than that of RUSY from the above characterizations, it presents a lower desorption (diffusion) rate than RUSY due to its higher acid density, reflecting the dominant role of the acidity effect on the molecular diffusion.

2.4. Catalytic Reaction Evaluation

The ultimate goal of the introduction of the mesopore and the adjustment of acidity for zeolites is to attain enhanced performance in catalytic reactions as a catalyst. In the present work, the catalytic efficiency of the modified FUSY and RUSY zeolites in MCH conversion was studied and compared with unmodified parent CPY, to provide insights into the relation between their BAS, pore structure, diffusion and catalytic performance. The MCH transformation is a model reaction of catalytic cracking which can be used to provide valuable information on acid sites and porosity of catalyst. A large number of studies have shown that the MCH transformation over solid acid catalysts is very complex and involves all the reactions during FCC: ring-opening, cracking, isomerization, hydride transfer reactions and coke formation [23,29].

Depending on the unmodified and different modification treatments, the conversion-versus-reaction time plots (Figure 5) show different behaviors. Though a fast initial decrease in the conversion followed by a quasi-plateau of activity is observed for the three samples, their difference is obvious. Firstly, modified FUSY and RUSY zeolites present much higher activity than unmodified CPY catalysts during the whole reaction time. At the initial stage of 5 min, the MCH conversion increases in the order of $CPY \ll RUSY < FUSY$, the order is exactly consistent with their strong BAS order and the latter two have strong MCH-conversion ability than the former due to the BAS accessibility of the latter two, although they have very close BAS amounts. When the reaction occurs, the ability of RUSY and FUSY in MCH-conversion tends toward unanimity, indicating better stability of RUSY and FUSY catalysts in the reaction than CPY because of diffusion. The product selectivity in the MCH conversion is directly dependent on the catalytic mechanism.

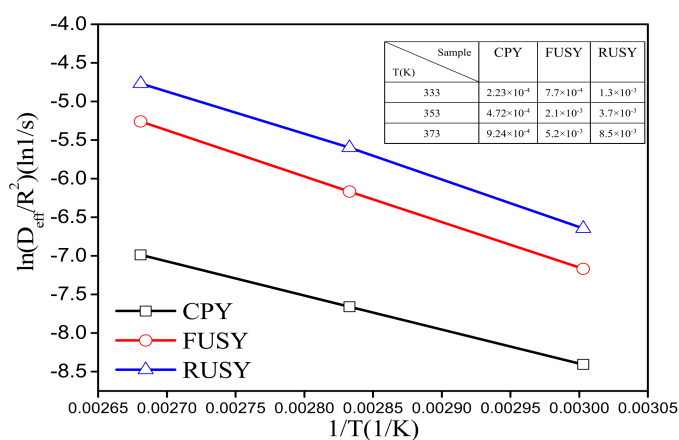


Figure 5. Evolution of methylcyclohexane (MCH) conversion versus reaction time on the three Y-zeolite catalysts.

Table 3 lists the product distribution of the three catalysts in the initial (5 min) and quasi-plateau (45 min) of the reaction. These products of MCH transformation are made up of three major types: cracking products (alkanes and alkenes in the range C_2 – C_7), isomers (dimethylcyclopentanes and ethylcyclopentane) and aromatics (benzene and toluene). As displayed in Figure 6, the selectivity (yield) to cracking, isomerization and aromatization calculated after 5 and 45 min of reaction show that whatever the zeolite sample and reaction time is, cracking and isomerization are the main reactions (>95%). In the initial stage, the selectivity for cracking products is higher than for isomerization ones. After 45 min of reaction, the isomerization product yield increases compared to cracking; that is, the contribution of strong BAS in the zeolite samples is decreased, accompanying the decreased activity, possibly due to the coking on the strong acid sites. In comparison with the parent CPY catalyst, the yield of cracking for modified FUSY and RUSY catalysts increases obviously; the tendencies are the same with the corresponding conversion and strong BAS accessibility and diffusion (an active region). Moreover, over the whole amount of cracking

products, C₃–C₇ hydrocarbons are the dominant components of all of the catalysts. Among them, isobutane (C₄) is the most abundant reaction product, and the changing trend of relative amounts depends on the yield to cracking.

Table 3. Product distributions at a reaction time of 5 and 45 min over the three Y-zeolite samples.

Products	5 min			45 min		
	CPY	FUSY	RUSY	CPY	FUSY	RUSY
C ₁ –C ₂	0.68	0.66	0.63	0.58	0.49	0.45
C ₃	3.03	6.20	5.00	2.10	3.28	3.06
C ₃ ⁼	0.64	0.47	0.38	0.49	0.38	0.31
iC ₄	11.2	19.0	14.0	6.11	9.29	8.81
nC ₄	1.68	3.39	2.80	1.10	1.79	1.70
iC ₄ ⁼	0.05	0.03	0.02	0.03	0.02	0.02
nC ₄ ⁼	0.23	0.14	0.13	0.17	0.13	0.11
C ₅	7.66	13.0	9.91	4.29	6.65	6.33
C ₅ ⁼	0.07	0.04	0.03	0.05	0.03	0.03
C ₆	9.52	13.2	11.7	5.69	8.47	8.62
C ₆ ⁼	1.25	2.61	1.82	0.73	1.24	1.05
C ₇	10.5	6.15	9.29	12.6	9.94	12.1
C ₇ ⁼	3.90	3.69	3.74	3.58	2.77	4.14
Isomers	48.2	27.6	35.6	58.2	51.6	49.4
Benzene	0.11	0.27	0.26	1.17	0.16	0.26
Toluene	1.37	3.64	4.67	3.06	3.78	3.61
Total	100	100	100	100	100	100
Cracking (C)	50.3	68.5	59.5	37.5	44.5	46.7
Isomers (I)	48.2	27.6	35.6	58.2	51.6	49.4
Aromatics (A)	1.48	3.91	4.93	4.23	3.94	3.87
Total	100	100	100	100	100	100

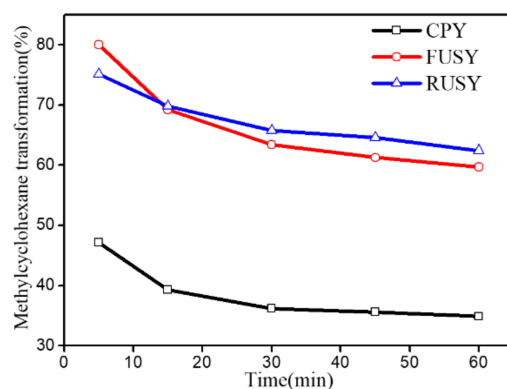


Figure 6. The product yield of three main types of products on the three Y-zeolite samples A: aromatics, I: isomerization products, C: cracking products.

The dominant mechanism of MCH conversion catalyzed by solid acids, known as the protolytic cracking (Haag-Dessau cracking mechanism), is now widely accepted [30–32]. MCH cracking can be initiated via the protonation of molecules, forming carbocation, the carbonium transition state, by the zeolitic BAS. The intermediate carbocations formed from protolytic cracking of ring or methyl side chain C–C bonds can react in several ways: desorption as heptane or heptene by proton and hydride transfer, isomerization and cracking before or after isomerization to give an alkene and alkane respectively, as well as methane and the products from the cyclohexyl carbenium ion. Alternatively, strong BAS can protonate a C–H bond for molecule MCH that contains tertiary hydrogens, giving methylcyclohexyl carbocation [33]. Once a methylcyclohexyl carbocation is formed, it can

crack by β -scission to produce products with less than seven carbons, primarily C_3 and i - C_4 alkene/alkane, isomerize to give alkylcyclopentanes and alkylcyclopentenenes, and lose hydrogens through a hydride transfer to finally produce toluene. Due to higher activation energy values for the first step of MCH cracking, i.e., the protonation of MCH molecules (Haag–Dessau mechanism), MCH conversion is dependent on both the concentration and strength of the acid sites [22,23]. The isomerization cracking and aromatization through hydrogen transfer are relatively acid strength demanding reactions, the activated complex that evolves into cracking products are different from the one leading to isomerization and dehydrogenation products. MCH isomerization followed by ring-opening and subsequent cracking is the main pathway, in which the cracking needs stronger acid sites than isomerization and dehydrogenation [34]. In addition to the acidity of zeolite, its pore structure also has an important effect on the conversion and product distributions of MCH conversion. The introduction of mesopore in zeolite can lead to an easier diffusion of the reactant and product molecules, further improving the catalytic activity of the Y-zeolite.

The order of the MCH conversion, as shown in Figure 5, is strictly parallel to the strong acid sites concentration derived from the pyridine-FTIR at 623 K, which confirms again the dependence of conversion on the strong acid sites; that is, the activity becomes higher with the amount of the strong acid sites increasing. On the other hand, the large enhancement obtained in the conversion over modified Y-zeolites is also due to the decrease of MCH molecular diffusion resistance from the increase of mesopore in the zeolite crystals. The enhanced diffusion ability is accompanied by an increased BAS accessibility to favor MCH cracking. Therefore, the high activity of FUSY and RUSY zeolites compared to CPY zeolite may be explained by the increase of strong BAS and an increase in the number of accessible sites from improved diffusion. In other words, a feasible “active region” (active site and location) can be adjusted for the isomerization, ring-opening and cracking reactions in MCH conversion. Whatever the type of zeolite sample, an initial decrease in the conversion can be observed—this deactivation is possibly due to the formation of bulky polyaromatic compounds (“coke”) on the strong BAS. This “coke” deposition induces a reduction of the active site concentration, especially strong BAS. The CPY catalyst had a large number of acid sites in BAS, LAS or total acid site amounts, but indicated a lower conversion ability to MCH and faster deactivation because of mass transfer limitations.

The synchronous trends for the product selectivity (and yield) to cracking with the conversion on all samples and reaction time are due to the dependence of cracking reaction toward strong Brønsted acid density. With a decrease in the number of strong BAS and cracking activities, the selectivity to isomerization increases.

The hydride transfer is defined as a bimolecular reaction in which a hydride is transferred between an alkane or alkene and a carbenium. The formation of toluene by hydride transfer requires three consecutive bimolecular reactions, which results in a very low aromatics yield on the three Y-zeolites. The relatively higher yields of the two modified zeolites than the parent zeolite may be associated with the presence of mesopores.

The relative selectivity of cracking products throughout the whole reaction is due to the stronger Brønsted acid sites on the FUSY and RUSY catalysts relative to the CPY catalyst by the Haag–Dessau cracking—the reactivity of heptane and heptene from the primary ring-opening products are enhanced on the FUSY and RUSY catalysts. For the same reason, more i - C_4 and C_3 products on the two modified catalysts can be attributed to the enhancing protolytic scission of dimethylcyclopentanes isomers followed by β -scission, which originated from the C–H bond cleavage. This result again proves the stronger acidity of the modified Y-zeolites than the parent Y, as the C–H bond cleavage requires stronger acid sites than the C–C bond cleavage.

3. Materials and Methods

3.1. Zeolite Samples

Three available Y-samples used in this study were provided by the Sinopec Dalian (Fushun) Research Institute of Petroleum and Petrochemicals. The commercial parent

Y-zeolite sample was named CPY, the modified CPY by ammonium fluorosilicate as FUSY, and then further treated zeolite by steaming as RUSY. The initial zeolite sample CPY was in the ammonium form, $\text{NH}_4\text{-Y}$. The resulting zeolite samples were calcinated to obtain H-zeolites.

3.2. Characterization Methods

Powder X-ray diffraction (XRD) was carried out on a SHIMADZU XRD-6000 diffractometer (Japan) with Cu $K\alpha$ radiation operating at 40 kV and 30 mA, respectively. The crystallinities and the framework Si/Al ratio of the samples were calculated according to the intensity of the peaks with a 2θ angle between $15\text{--}30^\circ$. Nitrogen adsorption/ desorption isotherms at 77 K were performed on a Quantachrome NOVA 1200e gas adsorption analyzer (America), and the samples were degassed at 373 K under vacuum for 4 h prior to adsorption analysis. The specific surface area (S_{BET}), micropore and mesopore volume of the samples were determined using the BET equation and NLDFT model, respectively. Field emission scanning electron microscope (SEM) images were obtained in a JEOL JSM-6700F instrument (Japan). The surface acidity was investigated by the pyridine-adsorbed FTIR technique. The self-supporting wafers were pretreated at 653 K in high vacuum conditions before pyridine adsorption to remove adsorbed water and other contaminants and to convert zeolites with ammonium form into hydrogen form.

3.3. Diffusion Study

Diffusion studies of MCH on the three Y-zeolite samples were performed on a zero-length column (ZLC) experimental apparatus [35]. Before each measurement, the zeolite sample of about 1–2 mg was sandwiched between two porous sintered metal discs placed into the ZLC column and activated overnight to eliminate impurities and moisture. During the measurement, the adsorbent was initially equilibrated with a low relative pressure of adsorbate, which was within the linear region of the adsorption isotherms, then followed by desorption with a high flow rate of He purge. The effluent concentration of the adsorbate was monitored by a flame ionization detector (FID), and the desorption curve was recorded by the computer. The ZLC response curve for spherical particles under isothermal conditions and linear equilibrium isotherm is given by the following:

$$\frac{C}{C_0} = 2L \sum_{n=1}^{\infty} \frac{\exp(-\beta_n^2 \frac{D_{\text{eff}}}{R^2} t)}{[\beta_n^2 + L(L-1)]} \quad (1)$$

where D_{eff}/R^2 is the effective diffusion time constant, R is the particle radius, L is a dimensionless parameter and β_n is eigenvalues given by the roots of the auxiliary equation:

$$\beta_n \cot \beta_n + L - 1 = 0 \quad (2)$$

and

$$L = \frac{1}{3} \frac{FR^2}{KV_s D_{\text{eff}}} \quad (3)$$

where F is the purge flow rate, V_s is the volume of adsorbent and K is the dimensionless Henry's law constant. Based on the above relationships, the D_{eff}/R^2 values can be obtained by fitting Equations (1)–(3) with the ZLC experimental data using MATLAB software.

3.4. Catalytic Tests

The catalytic tests for MCH conversion were conducted in a fixed-bed reactor (Tianjing, China) at ambient pressure of 623 K with nitrogen as a carrier gas ($P_{\text{Nitrogen}}/P_{\text{Methylcyclohexane}} = 7.2$). Before each experiment, the zeolite samples were crushed into 20–40 mesh particles and activated at 723 K for 12 h under N_2 flow. After the activation, the reaction was carried out for 60 min and products were collected from the reactor effluent at different reaction times, using a N_{itr} VICI 10-position valve (Switzerland) kept at 473 K. Finally, these samples were

analyzed by an Agilent 7890B gas chromatography (America) equipped with a HP-PLOT Al_2O_3 S (50 m, 0.53 mm diameter) capillary column and flame ionization detector.

4. Conclusions

In this paper, the catalytic transformations of methylcyclohexane (MCH) on the three Y-zeolites with a different framework of Si/Al ratios and mesoporous structures were conducted to reveal the influence of acidity and pore diffusion (“active region”) on catalytic activity and product distribution. The number of strong Brønsted acid sites in the modified FUSY and RUSY increased slightly compared with the parent CPY zeolite but indicated high MCH-conversion ability because of the improved mass transfer (ZLC desorption kinetic experiment results). The much-higher activity of the modified zeolites FUSY and RUSY in MCH conversion during the whole reaction was observed to be significant compared with the unmodified CPY due to the greater number of strong acid sites and enhanced pore diffusion upon modification. The catalytic results display that both the conversion and the cracking yield of MCH are greatly dependent on the strength and accessibility of acid sites inside zeolite; that is, the stronger the Brønsted strong acid site, the higher activity of the reactions. In addition, zeolite acidity has been shown to influence the selectivity of cracking products; the increased acid strength can enhance the reactivity of heptane and heptene from the primary ring-opening as well as the β -scission from the C–H bond cleavage, resulting in lesser C_7 products and more $i\text{-C}_4$ and C_3 products. The cracking and isomerization product yields are over 95%, which reveals that the mechanism is largely due to the Haag-Dessau cracking occurring during the conversion.

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References

1. Coronas, J. Present and future synthesis challenges for zeolites. *Chem. Eng. J.* **2010**, *156*, 236–242. [\[CrossRef\]](#)
2. Li, K.; Valla, J.; Garcia-Martinez, J. Realizing the commercial potential of hierarchical zeolites: New opportunities in catalytic cracking. *ChemCatChem* **2014**, *6*, 2754–2775. [\[CrossRef\]](#)
3. Primo, A.; Garcia, H. Zeolites as catalysts in oil refining. *Chem. Soc. Rev.* **2014**, *43*, 7548–7561. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Chal, R.; Gérardin, C.; Bulut, M.; van Donk, S. Overview and industrial assessment of synthesis strategies towards zeolites with mesopores. *ChemCatChem* **2011**, *3*, 67–81. [\[CrossRef\]](#)
5. Hartmann, M.; Machoke, A.G.; Schwieger, W. Catalytic test reactions for the evaluation of hierarchical zeolites. *Chem. Soc. Rev.* **2016**, *45*, 3313–3330. [\[CrossRef\]](#)
6. Schwieger, W.; Machoke, A.G.; Weissenberger, T.; Inayat, A.; Selvam, T.; Klumpp, M.; Inayat, A. Hierarchy concepts: Classification and preparation strategies for zeolite containing materials with hierarchical porosity. *Chem. Soc. Rev.* **2016**, *45*, 3353–3376. [\[CrossRef\]](#)
7. Wei, Y.; Parmentier, T.E.; De Jong, K.P.; Zecevic, J. Tailoring and visualizing the pore architecture of hierarchical zeolites. *Chem. Soc. Rev.* **2015**, *44*, 7234–7261. [\[CrossRef\]](#)
8. Zhang, K.; Ostraat, M.L. Innovations in hierarchical zeolite synthesis. *Catal. Today* **2016**, *264*, 3–15. [\[CrossRef\]](#)
9. Jiao, W.Q.; Fu, W.H.; Liang, X.M.; Wang, Y.M.; He, M.Y. Preparation of hierarchically structured Y zeolite with low Si/Al ratio and its applications in acetalization reactions. *RSC Adv.* **2014**, *4*, 58596–58607. [\[CrossRef\]](#)
10. García, J.R.; Bertero, M.; Falco, M.; Sedran, U. Catalytic cracking of bio-oils improved by the formation of mesopores by means of Y zeolite desilication. *Appl. Catal. A Gen.* **2015**, *503*, 1–8. [\[CrossRef\]](#)

11. De Jong, K.P.; Zecevic, J.; Friedrich, H.; De Jongh, P.E.; Bulut, M.; Van Donk, S.; Kenmogne, R.; Finiels, A.; Hulea, V.; Fajula, F. Zeolite Y crystals with trimodal porosity as ideal hydrocracking catalysts. *Angew. Chem. Int. Ed.* **2010**, *49*, 10074–10078. [[CrossRef](#)] [[PubMed](#)]
12. Garcia-Martinez, J.; Li, K.; Krishnaiah, G. A mesostructured Y zeolite as a superior FCC catalyst—From lab to refinery. *Chem. Commun.* **2012**, *48*, 11841–11843. [[CrossRef](#)] [[PubMed](#)]
13. Garcia-Martinez, J.; Johnson, M.; Valla, J.; Li, K.; Ying, J.Y. Mesostructured zeolite Y—High hydrothermal stability and superior FCC catalytic performance. *Catal. Sci. Technol.* **2012**, *2*, 987–994. [[CrossRef](#)]
14. Mihalyi, R.M.; Kollar, M.; Kiraly, P.; Karoly, Z.; Mavrodinova, V. Effect of extra-framework Al formed by successive steaming and acid leaching of zeolite MCM-22 on its structure and catalytic performance. *Appl. Catal. A Gen.* **2012**, *417*, 76–86. [[CrossRef](#)]
15. Verboekend, D.; Vile, G.; Perez-Ramirez, J. Mesopore formation in USY and Beta zeolites by base leaching: Selection criteria and optimization of pore-directing agents. *Cryst. Growth Des.* **2012**, *12*, 3123–3132. [[CrossRef](#)]
16. Kung, H.H.; Williams, B.A.; Babitz, S.M.; Miller, J.T.; Haag, W.O.; Snurr, R.Q. Enhanced hydrocarbon cracking activity of Y zeolites. *Top Catal.* **2000**, *10*, 59–64. [[CrossRef](#)]
17. Williams, B.A.; Babitz, S.M.; Miller, J.T.; Snurr, R.Q.; Kung, H.H. The roles of acid strength and pore diffusion in the enhanced cracking activity of steamed Y zeolites. *Appl. Catal. A Gen.* **1999**, *177*, 161–175. [[CrossRef](#)]
18. Lappas, A.A.; Patiaka, D.; Ikonomou, D. Separation and characterization of paraffins and naphthenes from FCC feedstocks. *Ind. Eng. Chem. Res.* **1997**, *36*, 3110–3115. [[CrossRef](#)]
19. Townsend, A.T. Fluid catalytic cracking: Science and technology. *Appl. Catal. A Gen.* **1994**, *109*, N16–N17. [[CrossRef](#)]
20. Abbot, J.; Wojciechowski, B.W. Kinetics of catalytic cracking of n-paraffins on HY zeolite. *J. Catal.* **1987**, *104*, 80–85. [[CrossRef](#)]
21. Benazzi, E.; Chapus, T.H.; Cheron, T.; Cauffriez, H.; Marcilly, C.H. Relationship between zeolite structure and hydrogen-transfer reactions in naphthenes and paraffins cracking. *Stud. Surf. Sci. Catal.* **1994**, *84*, 1663–1669.
22. Cerqueira, H.S.; Mihindou-Koumba, P.C.; Magnoux, P.; Guisnet, M. Methylcyclohexane transformation over HFAU, HBEA, and HMFI zeolites: I. reaction scheme and mechanisms. *Ind. Eng. Chem. Res.* **2001**, *40*, 1032–1041. [[CrossRef](#)]
23. Corma, A.; Mocholi, F.; Orchilles, V.; Koermer, G.S.; Madon, R.J. Methylcyclohexane and methylcyclohexene cracking over zeolite Y catalysts. *Appl. Catal.* **1990**, *67*, 307–324. [[CrossRef](#)]
24. Mihindou-Koumba, P.C.; Comparot, J.D.; Laforge, S.; Magnoux, P. Methylcyclohexane transformation over H-EU-1 zeolite: Selectivity and catalytic role of the acid sites located at the pore mouths. *J. Catal.* **2008**, *255*, 324–334. [[CrossRef](#)]
25. Martins, G.V.A.; Berlier, G.; Bisio, C.; Coluccia, S.; Pastore, H.O.; Marchese, L. Quantification of Brønsted acid sites in microporous catalysts by a combined FTIR and NH₃-TPD Study. *J. Phys. Chem. C* **2008**, *112*, 7193–7200. [[CrossRef](#)]
26. Schuring, D.; Koriabkina, A.O.; De Jong, A.M.; Smit, B.; van Santen, R.A. Adsorption and diffusion of n-hexane/2-methylpentane mixtures in zeolite silicalite: Experiments and modeling. *J. Phys. Chem. B* **2001**, *105*, 7690–7698. [[CrossRef](#)]
27. Vinh-Thang, H.; Huang, Q.L.; Ungureanu, A.; Eic, M.; Trong-On, D.; Kaliaguine, S. Structural and diffusion characterizations of steam-stable mesostructured zeolitic UL-ZSM-5 materials. *Langmuir* **2006**, *22*, 4777–4786. [[CrossRef](#)]
28. Vinh-Thang, H.; Huang, Q.L.; Ungureanu, A.; Eic, M.; Trong-On, D.; Kaliaguine, S. Effect of the acid properties on the diffusion of C₇ hydrocarbons in UL-ZSM-5 materials. *Micropor. Mesopor. Mater.* **2006**, *92*, 117–128. [[CrossRef](#)]
29. Al-Sabawi, M.; De Iasa, H. Kinetic modeling of catalytic conversion of methylcyclohexane over USY zeolites: Adsorption and reaction phenomena. *AIChE J.* **2009**, *55*, 1538–1558. [[CrossRef](#)]
30. Kotrel, S.; Knözinger, H.; Gates, B.C. The Haag–Dessau mechanism of protolytic cracking of alkanes. *Micropor. Mesopor. Mater.* **2000**, *35*, 11–20. [[CrossRef](#)]
31. Raichle, A.; Traa, Y.; Fuder, F.; Rupp, M.; Weitkamp, J. Haag–Dessau catalysts for ring opening of cycloalkanes. *Angew. Chem. Int. Edit.* **2001**, *40*, 1243–1246. [[CrossRef](#)]
32. Borm, R.V.; Reyniers, M.-F.; Martens, J.A.; Marin, G.B. Catalytic cracking of methylcyclohexane on FAU, MFI, and bimodal porous materials: Influence of acid properties and pore topology. *Ind. Eng. Chem. Res.* **2010**, *49*, 10486–10495. [[CrossRef](#)]
33. Martins, J.; Birot, E.; Guillon, E.; Lemos, F.; Ribeiro, F.R.; Magnoux, P.; Laforge, S. Sodium exchange over H-EU-1 zeolite. Part II: Catalytic properties. *Micropor. Mesopor. Mater.* **2013**, *171*, 238–245. [[CrossRef](#)]
34. Corma, A.; Agudo, A.L. Isomerization, dehydrogenation and cracking of methylcyclohexane over HNaY zeolites. *React. Kinet. Catal. Lett.* **1981**, *16*, 253–257. [[CrossRef](#)]
35. Liu, Z.; Fan, W.; Xue, Z.; Ma, J.; Li, R. Diffusion of n-alkanes in mesoporous 5A zeolites by ZLC method. *Adsorption* **2013**, *19*, 201–208. [[CrossRef](#)]