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Effect of external surface of HZSM-5 zeolite on product distribution in the conversion of methanol to hydrocarbons

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Abstract

The external surface of HZSM-5 zeolite was passivated by liquid siliceous deposition and by acidic sites poisoning with lepidine, respectively. Then methanol-to-hydrocarbons (MTH) reaction was investigated over the above as-prepared catalysts and the dissoluble coke on these used catalysts was analyzed by GC-MS, to study the role of the external surface of HZSM-5 in the catalytic reaction. Comparison with the experimental results based on parent ZSM-5 showed that the product distribution of MTH reaction was obviously influenced by the external surface. Evidences were listed as follows: (1) the final product on parent HZSM-5 showed higher aromatic selectivity, lower olefin selectivity, lower ratio of C_2/C_{3+} aliphatics and higher ratio of C_3/C_{4+} aliphatics than the reaction mixture produced by the sole catalysis of acidic sites in HZSM-5 channel; (2) a little of pentamethylbenzene and hexamethylbenzene in the product on parent HZSM-5, was produced via multi-methylation of methylbenzene on the external surface. The above conclusion may also be suitable for MTH reaction over other zeolites with 10-ring channel.

Key words
methanol-to-hydrocarbons; product distribution; HZSM-5; external surface; acidic sites

1. Introduction

As a key step in conversion of C1 sources to fuel and olefins, methanol-to-hydrocarbons (MTH) reaction on various zeolites has been extensively studied in the last several decades [1−8]. HZSM-5 zeolite is regarded as one of the most suitable catalytic materials, because of its regular pore and adjustable acidic properties. It has been widely accepted that MTH reaction follows dual-cycle mechanism in the channel of this zeolite [1,9−14]. Concretely, olefin-based cycle mainly produces C_{3+} olefins through repeated methylation-cracking of alkenes (not ethene) [9,11,15]; aromatic-based cycle not only forms low methylbenzenes, but also produces ethylene and some propylene through the demethylation of low methylbenzenes [16] and 1,2,4,5-tetramethylbezene [13,17]. Ethylene and C_{3+} olefins are separately formed [11,18], and aromatization of higher olefins is the bridge of the two cycles [1,13]. C_{2+} alkanes are mainly formed from olefins via hydrogen transfer reaction [9,19]. Methane can be formed via the decomposition and hydrogenolysis reactions of methanol and DME [20].

The conversion of methanol to propylene (MTP) and gasoline (MTG) using HZSM-5 zeolite as catalyst has achieved industrial application, but the byproducts (ethene and butenes for MTP, especially 1,2,4,5-tetramethylbenzene for MTG) can't be sufficiently eliminated yet [1]. Therefore, exact control of product selectivity has been the focus of the studies on MTH reaction over HZSM-5 catalyst at present. For example, it was found that the medium acidity was advantageous to the formation of light olefins, and propylene/ethylene ratio increased with the losing of strong acid sites [21−23] and the improvement of porous diffusion [24,25]. Phosphate-modified HZSM-5 catalyst increased the selectivity to C_2–C_4 alkenes [26]. Oligomerization and cracking of C_{3+} olefins showed influence on the distribution of C_{3+} aliphatics in the product at high methanol conversion, but had no effect on ethylene formation [27]. Besides, aromatization of methanol over HZSM-5 could be promoted by the interaction-dehydrogenation of surface metal oxides [28,29], such as ZnO, Ag_2O, CuO, Ga_2O_3 and SnO_2 etc. [30−35]. Coupling conversion of methanol with 2,5-dimethylfuran over HZSM-5 exhibited improved aromatic selectivity [36]. ZSM-5/MCM-48 composite zeolite showed excellent performance

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for MTG and MTA owing to mesoporous introduce [37,38]. Alkaline treatments improved the performance of HZSM-5 for MTG due to desilication and mesopore formation [39,40].

Although the dual cycle concept explains MTH reaction inside HZSM-5 channels well and great progress has been made in the control of product selectivity, the reactive behaviour on the external surface of this zeolite is not clear up to now. In general, HZSM-5 zeolite has considerable external surface with acid sites, high concentration of reactant, high rate of species transfer and no spatial confinement, which is usually an important place for secondary reaction [41−44]. Thus understanding of the role of the external surface of HZSM-5 zeolite in MTH reaction is very necessary, and it's likely to be helpful to the exact control of product selectivity.

Liquid silica deposition with polyphenylmethylsiloxane (PDMS) [45–47] and acidic sites poisoning with lepidine [48,49], are two effective methods for passivating the external surface of HZSM-5 without changing the internal surface. It can be attributed to that these modified reagents are too large in molecular size to enter the 10-ring channels. In this work, the external surface of HZSM-5 zeolite was passivated using the above two methods, respectively. Then, methanol-to-hydrocarbons was investigated over the as-prepared catalysts and the dissoluble coke on these used catalysts was analyzed. Comparison with the experimental results based on parent ZSM-5 showed that the product distribution of MTH reaction was obviously influenced by the external surface of this zeolite.

2. Experimental

2.1. Catalyst preparation

ZSM-5 zeolites with SiO_2/Al_2O_3 molar ratios of 50 and 200, were purchased from Shanghai Fuxu Company. Firstly, they were converted to NH_4-type ZSM-5 by conventional ion-exchange with aqueous NH_4NO_3 solution. Then, they were dried in an oven at 303 K and subsequently calcined at 813 K for 1 h with a ramp of 3 K/min, to obtain HZSM-5 zeolites. The H-type zeolites were pressed, crushed, and sorted to get parent HZSM-5 catalysts (particles of 12−20 mesh). The silica deposition was carried out by impregnation of parent HZSM-5 catalysts in liquid silicone PDMS (20 wt%) dissolved in petroleum ether. After complete volatilization of petroleum ether at room temperature, PDMS-modified HZSM-5 were calcined at 813 K for 1 h. This procedure was repeated four times to obtain the final catalysts, which were denoted as SiO_2-Z-50 and SiO_2-Z-200. Poisoning external acid sites of HZSM-5 was carried out by impregnating with solution of lepidine (20 wt%) in mesitylene. After twice washing with mesitylene and drying at 393 K for 6 h, Lpd-Z-50 and Lpd-Z-200 catalysts were obtained.

2.2. Characterization and analysis

The particle morphology of HZSM-5 zeolites was observed by means of scanning electron microscope (SEM, S-4800, Hitachi). The crystal structure of the prepared HZSM-5 catalysts was studied by X-ray diffraction analysis (XRD, D8ADVANCE) using Cu K_α radiation. The specific surface area and pore volume of samples were estimated by N_2 adsorption-desorption at 77 K (NOVA 2200e, Quantachrome, America). NH_3-TPD experiment was carried out on a conventional set-up equipped with a TCD (CHEMBET 3000). Infrared spectroscopy with pyridine adsorption (Py-IR) was obtained at 473 K and 673 K, respectively, with Pekin-Elmer 2000 FT-IR spectrometry and a self-supported wafer of sample. After eliminating aluminosilicate framework (used catalysts for 0.5 h reaction) with 15% HF, the composition of soluble coke extracted with CH_2Cl_2 was analyzed by GC-MS (Agilent 5973N). The constraint index (CI) was determined with a fixed-bed micro-reactor and hexane/3-methylpetane of 1/1 as the mixed reactants, 1.0 h^{-1} WHSV under total conversion 10%–60%, in the helium flow at atmosphere pressure. The products were analyzed using on-line gas chromatography (HP5890) with a 50 m HP-PLOT/Al_2O_3 "S" capillary column and FID, and the constraint index (CI) was calculated according to the reported method [50].

2.3. Catalytic reaction

3.0 g catalyst particles were packed into a stainless steel tubular fixed-bed reactor with 1.0 cm inner diameter. Methanol was pumped into the reactor by a metering pump. MTH reaction was carried out at 673 K, 1.0 h^{-1} WHSV and atmospheric pressure with a 40 mL/min N_2 flow. The reactor effluent was firstly analyzed online by a HP-5890 gas chromatograph equipped with a FID detector and a 50 m HP-FFAP capillary column, to know the distribution of aromatic products and the selectivity to total aliphatics. After passing a gas-liquid separator, the gas products were detailedly analyzed by a HP-5890 gas chromatograph equipped with a TCD detector and a 50 m HP-PLOT/Al_2O_3 "S" capillary column. Besides, the probe reactions, such as mesitylene conversion, toluene disproportionation and 1,2,4,5-tetramethylbenzene demethylation, were also carried out in the fixed-bed reactor at 673 K, 1.0 h^{-1} WHSV and atmospheric pressure with a 40 mL/min N_2 flow.

3. Results and discussion

3.1. Physicochemical properties of parent HZSM-5 and modified HZSM-5

SEM images for two HZSM-5 zeolites with different SiO_2/Al_2O_3 molar ratios are shown in Figure 1. As seen, both of them showed cubic crystal particles with the approximate sizes of 0.1−0.5 μm. This provided not only their similar distributions of external (the external surface of crystal particle) and internal (interior wall of channel) surfaces (as shown in Table 1), but also their similar diffusion-transfer properties. Thus it can be considered that SiO_2/Al_2O_3 molar ratio was the main factor which resulted in the difference in physicochemical properties of the two HZSM-5 zeolites. Moreover, parent HZSM-5 had large external specific surface area, more than 80 m^2/g. Besides, the external surface area and mesopore volume greatly decreased for modified HZSM-5, while their internal surface area and micropore volume almost kept constant. This implies that silica deposition and lepidine poisoning occurred only on the external surface. Figure 2 shows the XRD patterns of the prepared HZSM-5 catalysts. The peaks of modified catalysts were similar to those of parent HZSM-5, and no new diffraction peak appeared. This suggests that the structure of HZSM-5 was not destroyed and no new phase was produced during modification.

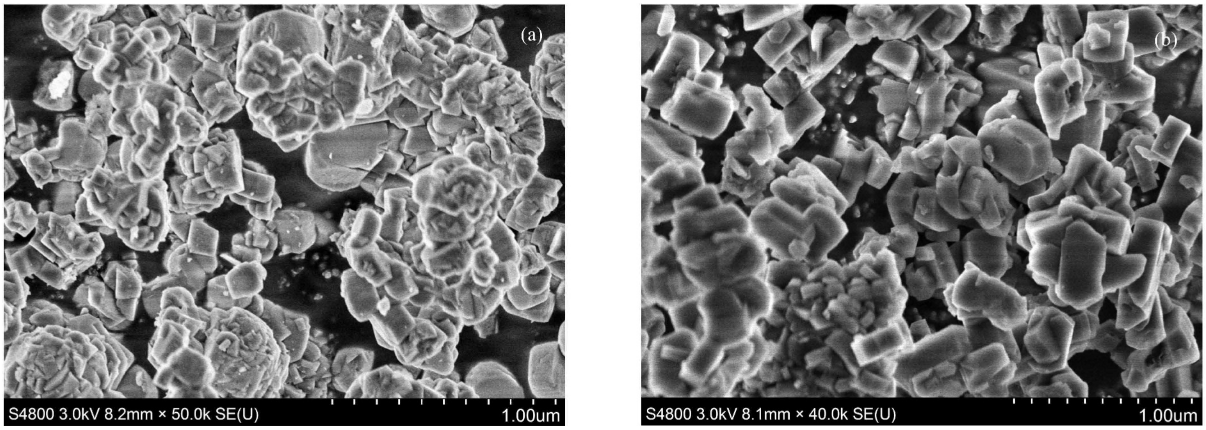

Figure 1. SEM images of HZSM-5 zeolites with different SiO_2/Al_2O_3 molar ratios. (a) $SiO_2/Al_2O_3 = 50$, (b) $SiO_2/Al_2O_3 = 200$

Table 1. Specific surface areas and pore volumes of parent HZSM-5 and modified HZSM-5

Catalysts	Specific surface area (m^2/g)			Pore volume (mL/g)	
	total (BET)	external	internal	mesopore	micropore
Parent Z-50	336	80	256	0.053	0.132
SiO_2-Z-50	271	20	250	0.027	0.128
Lpd-Z-50	277	25	252	0.029	0.130
Parent Z-200	343	85	258	0.060	0.134
SiO_2-Z-200	276	21	255	0.030	0.129
Lpd-Z-200	284	29	255	0.033	0.132

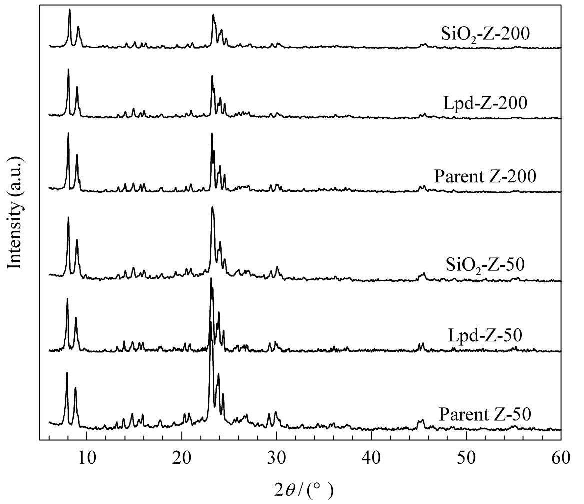

Figure 2. XRD patterns of parent HZSM-5 and modified HZSM-5

Due to the limited pore size of molecular sieve, mesitylene molecules are difficult to enter ZSM-5 channel [51]. Therefore, the mesitylene conversion was used to evaluate the change of the external surface acidity for the modified HZSM-5. Disproportionation of mesitylene only occurs on strong acid sites, while isomerization of mesitylene may take place on weak acid sites. Figure 3 displays the activity of mesitylene conversion over Lpd-modified HZSM-5 at different temperatures. The poisoned HZSM-5 could be significantly refreshed above 680 K owing to the desorption of lepidine. Thus 673 K was chosen to be the operative temperature for mesitylene conversion and MTH reaction, and to be the ceiling temperature for acid determination on Lpd-HZSM-5. As listed in Table 2, mesitylene conversion hardly took place over modified HZSM-5. This suggests that silica deposition and lepidine poisoning effectively eliminated the external acid sites on HZSM-5.

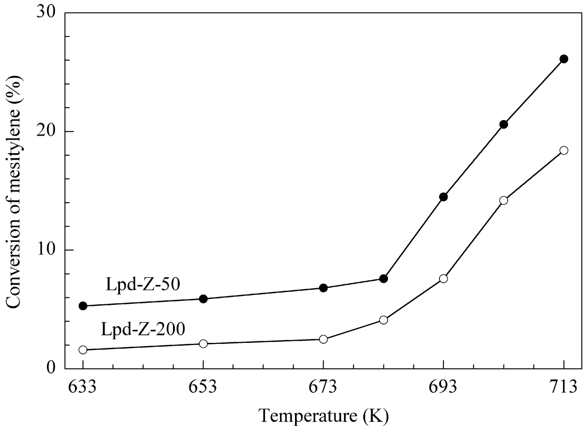

Figure 3. Influence of reaction temperature on mesitylene conversion over Lpd-modified HZSM-5. Mesitylene conversion was carried out in the fixed-bed reactor at 1.0 h^{-1} WHSV and atmospheric pressure with a 40 mL/min N_2 flow. Data were obtained at 0.5 h

Table 2. Results for mesitylene conversion over parent HZSM-5 and modified HZSM-5

Catalysts	Mesitylene conversion (%)*		
	total conversion	disproportionation	isomerization
Parent Z-50	46.9	9.7	37.2
SiO_2-Z-50	7.6	1.3	6.3
Lpd-Z-50	6.8	0.9	5.9
Parent Z-200	37.4	3.3	34.1
SiO_2-Z-200	5.4	0.7	4.7
Lpd-Z-200	2.5	0.5	2.0

* Mesitylene conversion was carried out in the fixed-bed reactor at 673 K, 1.0 h^{-1} WHSV and atmospheric pressure with a 40 mL/min N_2 flow. Data were obtained at 0.5 h

NH_3-TPD and Py-IR results of the prepared HZSM-5 catalysts are shown in Figure 4, Table 3 and Table 4. As seen, modified HZSM-5 showed lower acidic density and lower acidic strength than parent HZSM-5 owing to the significant loss of external acid sites. This implies that strong acid sites on external surface were preferential to be eliminated by the two kinds of modifications. As a result, the external acidity was very weak for the modified HZSM-5, although a little of weak acid sites still remained there. While the internal acidity was hardly influenced, thus the total acidic density of the modified HZSM-5 reflected by NH_3-TPD and Py-IR was still high. Furthermore, parent Z-200 and modified Z-200 showed lower acidic density than the corresponding Z-50 catalysts, respectively, due to the higher SiO_2/Al_2O_3 molar ratio of Z-200. This is in agreement with the results of mesitylene conversion test, as shown in Table 2. In addition, as shown in Table 4, the decrease in the ratio of Brønsted/Lewis (B/L) acid sites after modification suggests that external B acid sites were preferential to be eliminated by silica deposition and lepidine poisoning.

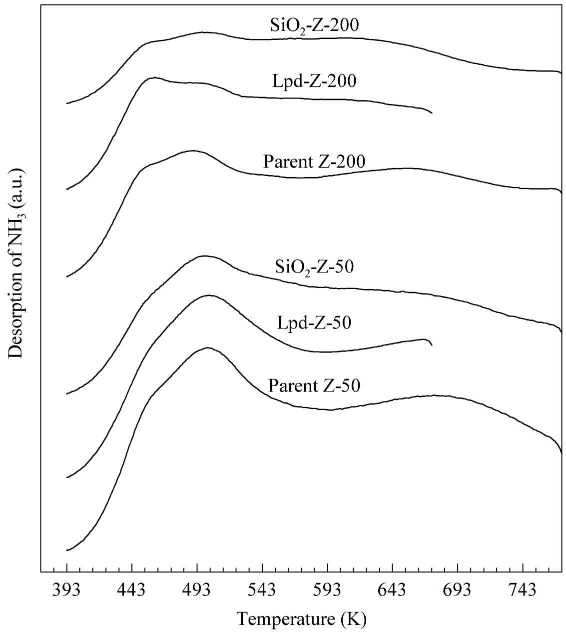

Figure 4. NH_3-TPD profiles of parent HZSM-5 and modified HZSM-5

Table 3. Data obtained from NH_3-TPD on parent HZSM-5 and modified HZSM-5

Catalysts	Desorbed NH_3 (mmol/g)	
	393−573 K (weak acid sites)	573−773 K (strong acid sites)
Parent Z-50	0.64	0.47
SiO_2-Z-50	0.45	0.26
Lpd-Z-50	0.48	0.18
Parent Z-200	0.28	0.21
SiO_2-Z-200	0.19	0.11
Lpd-Z-200	0.24	0.12

Table 4. Py-IR results of parent HZSM-5 and modified HZSM-5

Catalysts	B acid sites		L acid sites		B/L
	473 K	673 K	473 K	673K	ratio
Parent Z-50	3.67	1.16	0.88	0.31	4.17
SiO_2-Z-50	2.83	0.87	0.70	0.24	4.04
Lpd-Z-50	2.03	0.25	0.66	0.24	3.08
Parent Z-200	1.46	0.33	0.52	0.29	2.81
SiO_2-Z-200	1.03	0.22	0.41	0.23	2.51
Lpd-Z-200	1.18	0.23	0.46	0.27	2.57

The number of acid sites is a relative value of Brønsted acid sites to Lewis acid sites, estimated by the corresponding calibrated peak area

As the industrial processing for high-selective production of p-xylene, shape-selective toluene disproportionation has been fully understood over modified HZSM-5 catalyst. The high selectivity to p-xylene is due to the external surface passivation and narrowing porous opening [44]. Because the p-xylene formed inside channels hardly isomerizes after diffusing to the external surface passivated, and its isomers can't diffuse out owing to the shape-selectivity of narrowed pore-opening, toluene disproportionation was used to evaluate the changes of pore-opening size and external surface acidity for modified HZSM-5 in this work. Besides, 1,2,4,5-tetramethylbenzene is the largest hydrocarbon able to diffuse in HZSM-5 pores [16], and its demethylation was also used to evaluate the change of pore-opening size for modified HZSM-5.

Table 5. Selectivity to p-xylene in toluene disproportionation under the nearly same conversion over parent HZSM-5 and modified HZSM-5

Catalysts	Reaction temperature (K)	Conversion of toluene (%)	Selectivity to p-xylene (%)
Parent Z-50	633	14.6	23.5
SiO_2-Z-50	723	14.3	94.8
Lpd-Z-50	673	15.8	53.9
Parent Z-200	643	2.9	23.1
SiO_2-Z-200	733	3.6	95.7
Lpd-Z-200	673	3.4	45.7

Toluene disproportionation was carried out in the fixed-bed reactor at 1.0 h^{-1} WHSV and atmospheric pressure with a 40 mL/min N_2 flow. Data were obtained at 0.5 h. Selectivity to p-xylene: the selectivity of p-xylene in xylene

As shown in Figure 5 and Table 5, p-xylene selectivity was about 23%–24%, a thermodynamic equilibrium value, over parent HZSM-5. However, SiO_2-modified HZSM-5 showed above 94% selectivity owing to their weak external acidity and narrow pore-opening [44,45,47]. Remarkably, Lpd-modified HZSM-5 exhibited lower p-xylene selectivity than SiO_2-HZSM-5 with the same SiO_2/Al_2O_3 molar ratio, but higher than parent HZSM-5. However, Lpd-modified HZSM-5 showed lower activity for mesitylene conversion than SiO_2-HZSM-5. Moreover, as shown in Figure 6, the demethylation of 1,2,4,5-tetramethylbenzene hardly occurred over SiO_2-HZSM-5, while its activity still remained at high level over Lpd-HZSM-5. These results imply that lepidine poisoning only neutralized the external acid sites, but hardly enhanced the diffusion limitation at the porous opening of HZSM-5 zeolite.

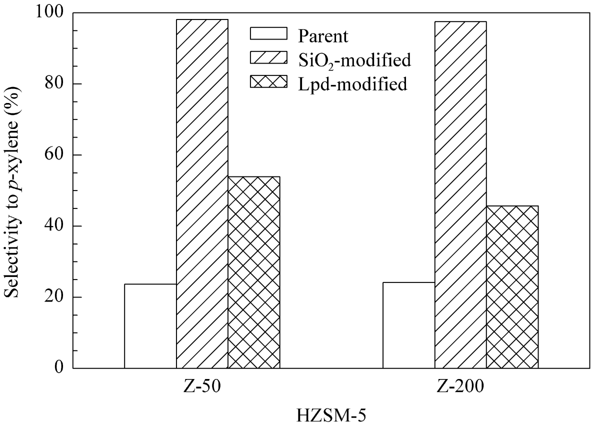

Figure 5. Selectivity to p-xylene in toluene disproportionation over parent HZSM-5 and modified HZSM-5. Toluene disproportionation was carried out in the fixed-bed reactor at 673 K, 1.0 h^{-1} WHSV and atmospheric pressure with a 40 mL/min N_2 flow. Data were obtained at 0.5 h. Selectivity to p-xylene: the selectivity to p-xylene in xylene

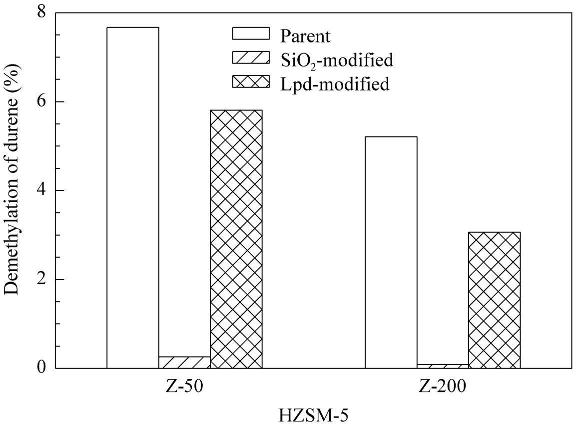

Figure 6. The activity of 1,2,4,5-tetramethylbenzene demethylation over parent HZSM-5 and modified HZSM-5. 1,2,4,5-tetramethylbenzene demethylation was carried out in the fixed-bed reactor at 673 K, 1.0 h^{-1} WHSV and atmospheric pressure with a 40 mL/min N_2 flow. Data were obtained at 0.5 h

Constraint index (CI) is an effective method to determinate the porous size of zeolite, based on the cracking reaction of probe molecules [43]. Thus the pore-opening properties of HZSM-5 before or after modification were also characterized by CI determination. As shown in Table 6, the CI values of SiO_2-modified HZSM-5 were higher than those of parent and Lpd-modified HZSM-5, while the two latter HZSM-5 catalysts showed the near value. This again proves the different pore-opening size of SiO_2-HZSM-5 and Lpd-HZSM-5 reflected by the above probe reactions, such as toluene disproportionation and demethylation of 1,2,4,5-tetramethylbenzene.

Table 6. The constraint index (CI) of parent HZSM-5 and modified HZSM-5

Catalysts	Parent Z-50	SiO_2-Z-50	Lpd-Z-50	Parent Z-200	SiO_2-Z-200	Lpd-Z-200
CI value	6.0	8.8	6.3	6.1	9.0	6.2

3.2. Effect of external surface of HZSM-5 zeolite on product distribution of MTH reaction

MTH reaction was investigated over parent HZSM-5 and modified HZSM-5. As seen in Figure 7, the catalytic stability of the prepared HZSM-5 catalysts was compared in the reaction for 5 h. Owing to the strong acidity inside channel, obvious deactivation occurred for modified Z-50. Especially, the conversion of methanol, aliphatic yield and aromatic yield significantly decreased over SiO_2-Z-50 during 0.75−2.0 h. This could result from the fast formation of large-size coke molecules (such as large aromatics and lager olefins) inside the bottle-shaped channels [47]. Although there was no difference in the diffusion limitation at the porous opening on parent Z-50 and Lpd-Z-50, the conversion of methanol and aromatic yield still declined obviously during 1.0−5.0 h reaction over the latter catalyst. This may be related to the higher methanol concentration inside the channels of Lpd-Z-50, which favors coke formation on strong acid sites [47], because a part of methanol must be consumed by the reaction on external surface before it diffuses into the channels of parent HZSM-5. With the invalidation of internal strong acid sites during the deactivation of modified Z-50, aromatization and hydrogen transfer reaction were weakened, and olefin selectivity significantly increased. Besides, the aromatic yield also decreased with the increasing reaction time (1.0−5.0 h) over parent Z-50, while aliphatic yield and olefin selectivity increased. However, no obvious changes for methanol conversion, hydrocarbon yield and olefin selectivity were observed during the whole reaction for 5 h over parent and modified Z-200, due to their weak acidity which can suppress coke formation. Above results indicate that relatively serious coke deposition can cover much strong acid sites and influence the product distribution of this reaction over HZSM-5 zeolite. This is in agreement with the experimental result reported by Wang et al. [23]. Therefore, in the present work, the products of MTH at 0.5 h over the prepared HZSM-5 catalysts were chosen to analyze in detail, to exactly study the reactive behaviour on the external surface of HZSM-5 zeolite.

Table 7 shows the detailed results of MTH reaction at 0.5 h over the prepared HZSM-5 catalysts. Modified HZSM-5 which lost most of external acid sites showed lower methanol conversion than parent HZSM-5. Besides, compared with the product distribution on parent HZSM-5, obvious changes were observed on the modified catalysts. The change trends for the two HZSM-5 zeolites with different SiO_2/Al_2O_3 molar ratios were accordant, although Z-200 series catalysts showed lower aromatic selectivity but higher aliphatic selectivity due to their weaker acidity [52]. Moreover, the differences of p-xylene selectivity between parent HZSM-5 and modified HZSM-5 here were in agreement with those in toluene disproportionation at the same temperature shown in Figure 5. This also proves our understanding of the external surface acidity and pore-opening size of modified HZSM-5 in Section 3.1. These results strongly suggest that the external surface of HZSM-5 zeolite plays an important role in MTH reaction.

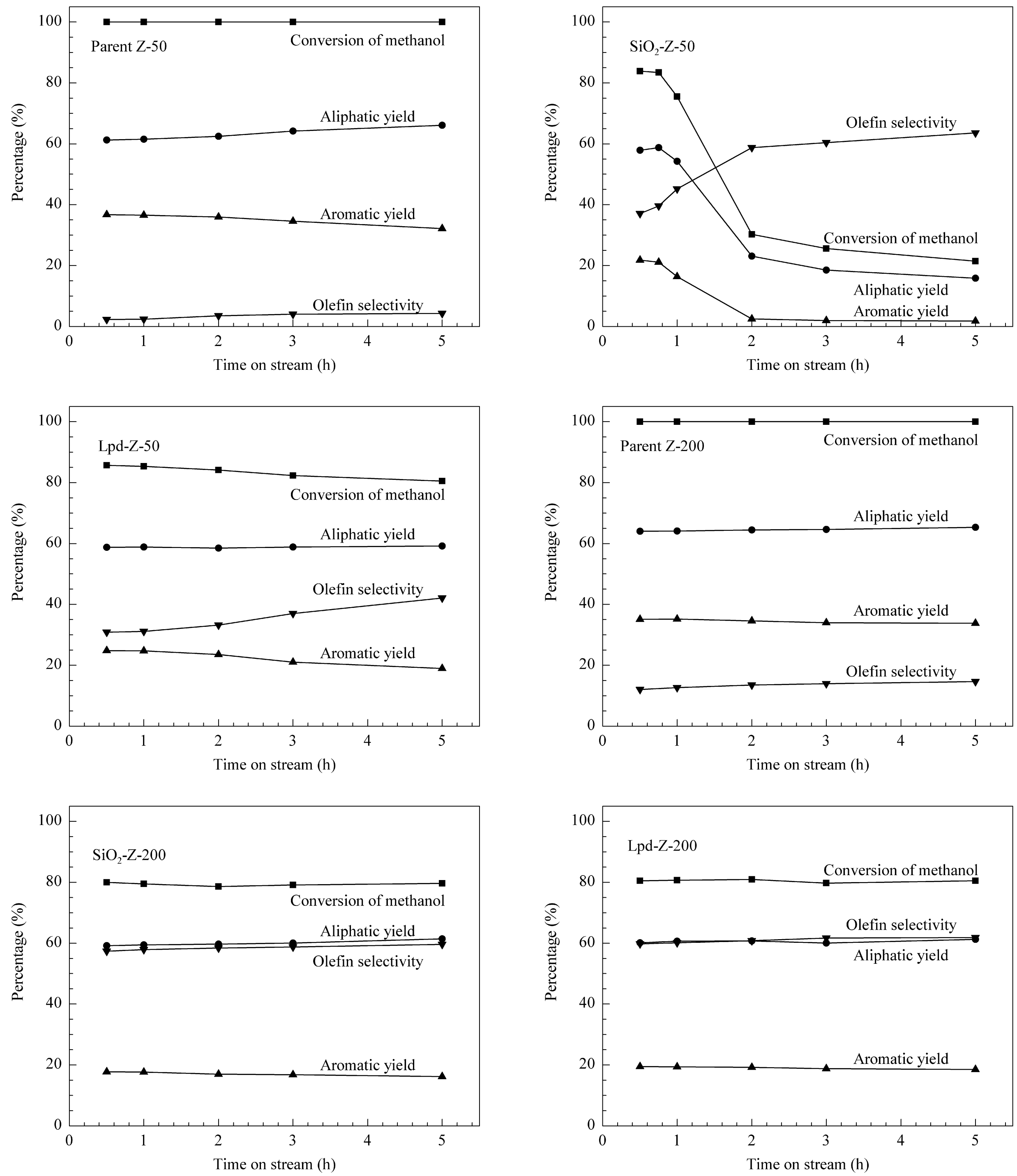

Figure 7. The catalytic stability of parent and modified HZSM-5 in MTH reaction for 5 h. MTH reaction was carried out at 673 K, 1.0 h^{-1} WHSV and atmospheric pressure with a 40 mL/min N_2 flow. Olefin selectivity: the selectivity of olefin in hydrocarbons

Table 7. Detailed results of MTH reaction at 0.5 h over parent HZSM-5 and modified HZSM-5

	Parent Z-50	SiO_2-Z-50	Lpd-Z-50	Parent Z-200	SiO_2-Z-200	Lpd-Z-200
Methanol conversion (%)	99.99	83.84	85.65	99.99	79.94	80.46
Hydrocarbon yield (wt%)	98.03	79.75	83.59	99.19	77.01	79.58
Distribution of hydrocarbon products (wt%)						
Methane	7.00	10.21	9.04	7.15	10.61	9.22
Ethane	5.82	2.63	2.76	2.78	0.90	0.47
Ethylene	1.45	19.98	17.39	4.27	18.62	17.59
Propane	40.03	15.75	18.43	31.60	3.49	2.27
Propene	0.69	13.96	10.36	6.54	28.21	30.15
Butane	6.63	5.76	7.04	9.15	3.28	2.43
Butene	0.17	2.36	2.69	1.04	8.52	9.52
C_{5+} aliphatics	0.75	1.94	2.57	2.03	3.25	3.85
Benzene	7.94	7.04	7.30	8.34	5.89	6.19
Toluene	9.45	8.93	9.02	9.81	7.01	7.48
Xylene	12.54	9.45	9.64	12.25	8.82	9.05
Trimethylbenzene	2.03	0.15	0.41	1.55	0.04	0.38
1,2,4,5-Tetramethylbenzene	0.16	0	0.09	0.06	0	0.04
Other tetramethylbenzenes	0.23	0	0	0.09	0	0
Pentamethylbenzene	0.33	0	0	0.02	0	0
Hexamethylbenzene	0.07	0	0	0.03	0	0
Naphthalenes	2.11	0.39	1.50	1.35	0.43	0.52
Other aromatics	2.60	1.45	1.76	1.94	0.93	0.84
Total aliphatics	62.54	72.59	70.28	64.56	76.88	75.50
Total aromatics	37.46	27.41	29.72	35.44	23.12	24.50
p-Xylene selectivity (%)	23.98	98.06	52.86	24.15	96.31	44.27

p-Xylene selectivity: p-xylene selectivity in xylene products

As shown in Table 7, owing to the passivation of external surface, Lpd-HZSM-5 showed higher aliphatic selectivity but lower aromatic selectivity than parent HZSM-5. This implies that aromatization of higher olefins also took place on external surface. Surprisingly, the selectivity to olefins significantly increased over modified HZSM-5, while that of alkanes decreased. This phenomenon indicates that external surface is an important place for the formation of alkanes.

C_{2+} alkanes are mainly formed from corresponding olefins via hydrogen transfer reaction. Moreover, ethylene is predominantly produced by aromatic-based cycle, while C_{3+} olefins are mainly formed via repeated methylation-cracking in olefin-based cycle. Therefore, the ratios of C_2/C_{3+} aliphatics and C_3/C_{4+} aliphatics were used to reflect the reactive behaviour on the external surface further. As seen in Figure 8, modified HZSM-5 showed higher ratio of C_2/C_{3+} aliphatics but lower ratio of C_3/C_{4+} aliphatics than parent HZSM-5 with the same SiO_2/Al_2O_3 molar ratio. This result indicates that the changes of aliphatic distribution on modified catalysts were mainly caused by suppressing the catalytic reactions on external surface, but not resulted from shape-selectivity of porous opening. Then, it can be confirmed that the reactive actions on external surface result in relatively low ratio of C_2/C_{3+} aliphatics but high ratio of C_3/C_{4+} aliphatics in the final product over parent HZSM-5.

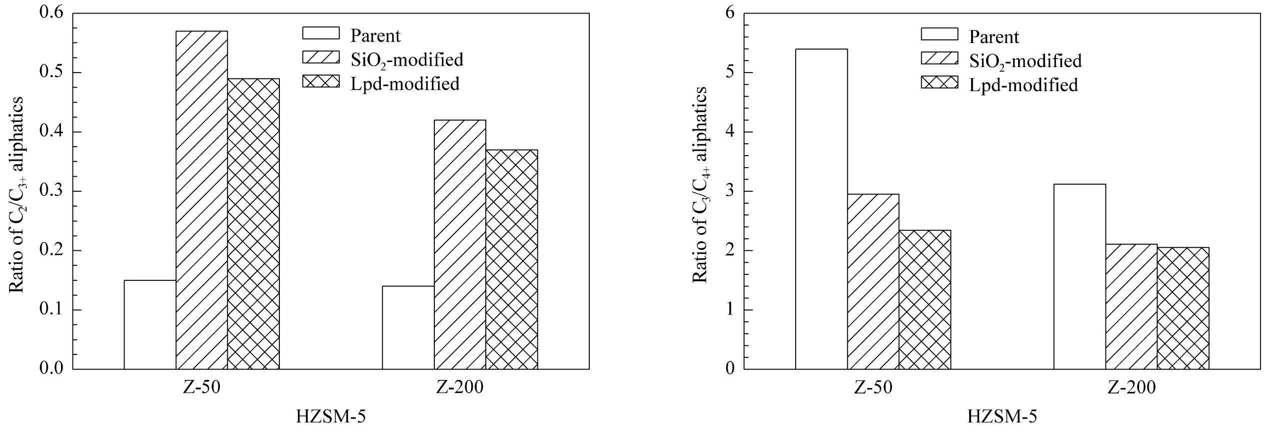

Figure 8. Ratios of C_2/C_{3+} aliphatics and C_3/C_{4+} aliphatics for the products of MTH reaction at 0.5 h over parent HZSM-5 and modified HZSM-5

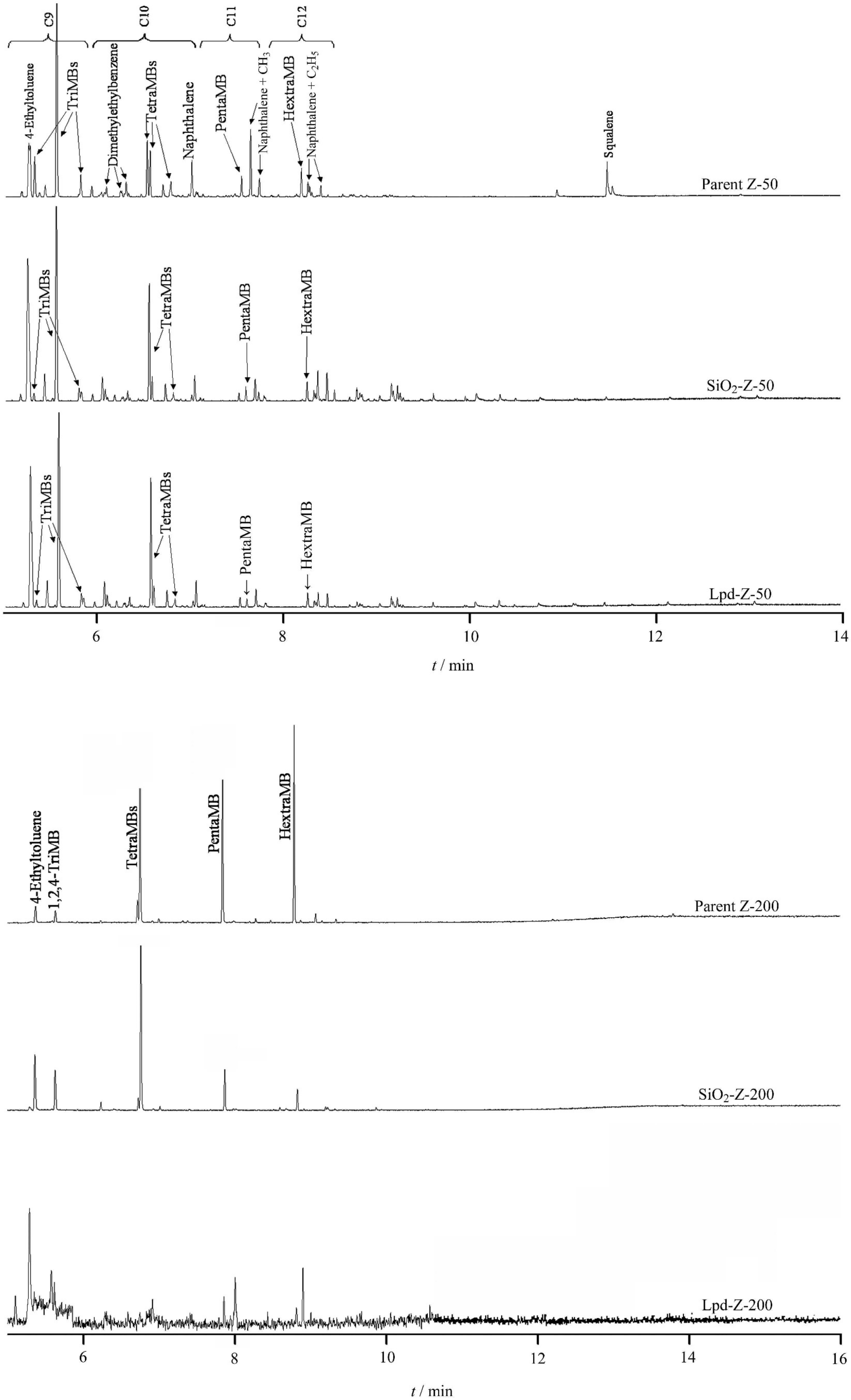

Figure 9. GC-MS analytical results of dissoluble coke on used parent HZSM-5 and used modified HZSM-5 in MTH reaction for 0.5 h

Most of low methylbenzenes and light olefins formed inside HZSM-5 channel must diffuse to the external surface. However, low methylbenzenes show lower diffusion rate owing to the diffused restriction of micropore. Thus, light olefin molecules in channel are easier to diffuse to the external surface with high methanol concentration. Comparing with ethylene, C_3–C_5 olefins have much higher reactivity for methylation to form higher olefins [13,53,54]. Then, there is not only aromatization and hydrogen transfer reaction on the external surface without spatial confinement, but also much extra C_3–C_5 olefins are produced via the cracking of higher olefins there. As a result, the final product over parent HZSM-5 showed higher aromatic selectivity, lower olefin selectivity, lower ratio of C_2/C_{3+} aliphatics and higher ratio of C_3/C_{4+} aliphatics than the reaction mixture produced by the sole catalysis of acidic sites in HZSM-5 channel. In addition, SiO_2-HZSM-5 showed lower aromatic selectivity and higher ratio of C_2/C_{3+} aliphatics than Lpd-modified HZSM-5 with the same SiO_2/Al_2O_3 molar ratio. This is mainly due to the stronger diffusion restriction on aromatic molecules at the narrowed pore-opening on SiO_2-HZSM-5. The extension of retention time of aromatic molecules can result in a relatively enhanced low methylbenzene cycle, producing ethylene inside the bottle-shaped channels [55].

As listed in Table 7, there were some pentamethylbenzene and hexamethylbenzene in the effluent product over parent HZSM-5. However, they were not detected in the product over modified HZSM-5, although the selectivities to benzene, toluene and xylene still remained at a high level. Besides, as seen in Figure 9, the relative contents of these multi-methylbenzenes in the dissoluble coke on the used modified HZSM-5 were much lower than those on the used parent HZSM-5. Moreover, although these multi-methylbenzenes can be formed at the channel crossings of HZSM-5 in this reaction, they are stuck and virtually unreactive [16]. These facts strongly suggest that a little of pentamethylbenzene and hexamethylbenzene in the product over parent HZSM-5, were produced via multi-methylation of methylbenzene on the external surface.

Based on all the above findings, it can be summarized that the product distribution of MTH reaction is greatly influenced by the external surface of HZSM-5 zeolite. That's why the compositions of the products over SiO_2-HZSM-5 and Lpd-HZSM-5 were significantly different from that over parent HZSM-5.

4. Conclusions

The external surface of HZSM-5 zeolite was passivated by liquid siliceous deposition and acidic sites poisoning with lepidine, respectively. Then both parent and modified HZSM-5 were tested by methanol-to-hydrocarbons (MTH) reaction, and the dissoluble coke on these used catalysts was also analyzed. It was found that the final products on parent HZSM-5 showed higher aromatic selectivity, lower olefin selectivity, lower ratio of C_2/C_{3+} aliphatics and higher ratio of C_3/C_{4+} aliphatics than the reaction mixture produced by the sole catalysis of acidic sites in HZSM-5 channel. Moreover, a little of pentamethylbenzene and hexamethylbenzene in the final product were produced via multi-methylation of methylbenzene on the external surface. Therefore, it can be confirmed that the product distribution of MTH reaction is greatly influenced by the external surface of HZSM-5 zeolite. This conclusion can provide guidance for the exact control of product selectivity over HZSM-5 catalyst, and it may also be suitable for MTH reaction over other zeolites with 10-ring channel.

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