Improved Selectivity toward Light Olefins in the Reaction of Toluene with Methanol Over the Modified HZSM-5 Catalyst

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Light olefins and *para*-xylene were produced with high selectivity in the reaction of toluene with methanol over a modified HZSM-5 catalyst. Ordered mesoporous structure and weaker acidic sites led to significant contribution to the selectivity toward *para*-xylene. By means of a single-pulse reaction and the temperature-programmed surface reaction, it was confirmed that the presence of toluene and as-produced xylene shortened the reaction induction period and reduced the formation temperature of ethylene and propylene, which was beneficial to improve the selectivity toward light olefins, particularly ethylene.

para-Xylene (PX) is one of the important organic materials used for the synthesis of pure terephthalic acid, which is used to make polyesters, particularly polyethylene terephathalate. In industrial processes, PX is produced from the aromatics of a naphtha catalytic reformer through complicated crystallization or adsorption separation; this method is very costly to obtain the desired purity of more than 99%. The selective alkylation of toluene with methanol over the modified HZSM-5 catalyst has been studied extensively for decades. In general, steam treatment,[1] poison treatment of large molecules,[2] modification of Mg,[3, 4] B,[5] P,[6] La,[7] Pt,[8] and so forth, and silylation method[9, 10] were used to improve porous and acidic properties of the HZSM-5 catalyst to produce PX in concentrations greater than equilibrium concentrations. In addition, methanol reacted partially with toluene to produce alkylbenzenes and the rest was dehydrated to form hydrocarbons by using the methanol-to-hydrocarbon (MTH) process.[11] Some studies focused on improving the alkylation reaction as well as restraining side reactions. Thus, a high toluene/methanol molar feed ratio was often used, which would result in low conversion of toluene. However, light olefins, particularly ethylene and propylene, among hydrocarbons were not useless. They were important chemicals for the production of polyethy-

lene and polypropylene, and ethylene was also a major component for the production of polyethylene terephathalate. Therefore, it would be meaningful to improve toluene conversion by using an optimum feed ratio of toluene and methanol, to restrain the formation of undesired aromatics with a designed catalyst, as well as to transform the excess methanol (unreacted with toluene) to important chemicals under the same conditions. Hence, we proposed a new mechanism to produce PX with use of extremely high-purity and high-concentration ethylene and propylene in one chemical reaction through the transformation of toluene and methanol (Scheme 1) over the modified HZSM-5 catalyst. It was also of great significance that the two materials used for the production of polyesters—PX and ethylene—could be obtained in one chemical reaction.
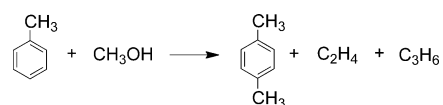
Scheme 1. A new mechanism for the transformation of toluene and methanol.

The modified HZSM-5 catalyst for this process is expected to function in two transformations: one is the alkylation of toluene with methanol to produce PX with high selectivity and the other is the conversion of methanol to high-concentration ethylene and propylene. Therefore, the Si/PLaHZSM-5 catalyst was designed by using a progressive modification method to improve the acidity and channel character. The XRD patterns of HZSM-5 and Si/PLaHZSM-5 catalysts, in which peak positions matched the characteristics of the MFI structure, are shown in Figure 1a. The diffraction peak intensity of the Si/PLaHZSM-5 catalyst decreased at $2\theta = 23.0–24.3°$, which indicated that the crystal structure corresponding to that lattice spacing changed after the modification. A new signal at $2\theta = 7.2°$ appeared, which was possibly due to the phase transformation of the HZSM-5 catalyst.[12] N_2 physisorption isotherms of HZSM-5 and Si/PLaHZSM-5 catalysts are shown in Figure 1b. For the HZSM-5 catalyst, the adsorption and desorption branches of the isotherm coincided with each other and no hysteresis loop was observed; this finding was attributed to a type I isotherm typical of microporous materials. For the Si/PLaHZSM-5 catalyst, the adsorption feature in microporous materials was well maintained and the desorption branch of the isotherm demonstrat-

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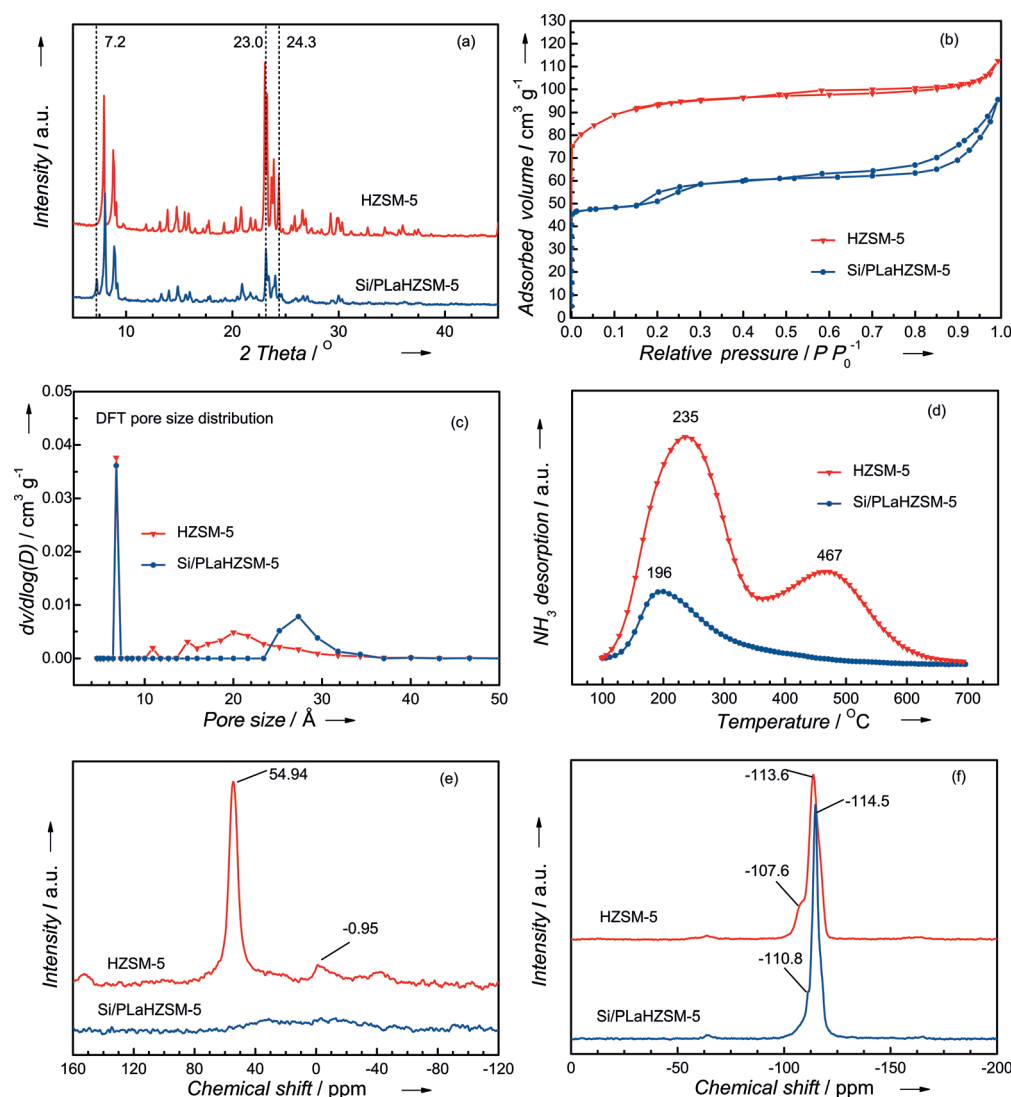Beijing 100049 (P.R. China)

Figure 1. a) XRD patterns, b) N_2 physisorption isotherms, c) pore size distribution, d) NH_3-temperature programmed desorption profiles, and e) ^{27}Al and f) ^{29}Si MAS NMR spectra of HZSM-5 and Si/PLaHZSM-5 catalysts.

sieve.[13] In addition, the improvement in the thermal stability of the HZSM-5 catalyst during the P/La modification prevented the removal of framework Al atoms in steaming treatment.[14] Therefore, many weaker acidic sites were left even after silanization modification, and owing to the coverage and migration of the SiO_2 layer, the acidic strength was reduced. The ^{27}Al and ^{29}Si MAS NMR spectra of HZSM-5 and Si/PLaHZSM-5 catalysts are shown in Figure 1e and f. The chemical shifts at 54.94 and −0.95 ppm in the ^{27}Al MAS NMR spectrum of the HZSM-5 catalyst were ascribed to tetrahedral framework Al and six-coordinated extra-framework Al species, respectively. The chemical shifts at 113.6 and −107.6 ppm in the ^{29}Si MAS NMR spectrum of the HZSM-5 catalyst were ascribed to Si(0Al) and Si(1Al) species, respectively. After the modification, the intensity of resonance peaks of both tetrahedral framework Al and six-coordinated extra-framework Al species was weakened and the broadening and shifting of resonance peaks to high field were observed. However, the intensity of resonance peaks of Si(0Al) and Si(1Al) species was improved and the narrowing and shifting of resonance peaks to high field

were observed. These results illustrated that dealuminated silicon-enriched zeolite was obtained,[15] and ordered lattice arrangement and regular framework structure were confirmed further.[16]
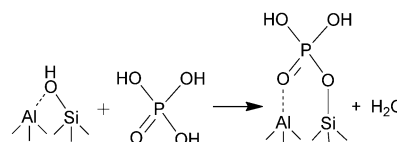
Scheme 2. The formation of P hydroxyl.

The reaction of toluene with methanol was performed over HZSM-5 and Si/PLaHZSM-5 catalysts in a fixed-bed reactor, with the toluene/methanol feed molar ratio ranging from 0:1 to 2:1. All effluents were kept warm and analyzed online with

ed two hysteresis loops in the relative pressure range of 0.15–0.35 and 0.50–0.90, respectively, which was similar to the type IV isotherm observed for the mesoporous structure of MCM-41. This fact could also be observed in the pore size distribution of HZSM-5 and Si/PLaHZSM-5 catalysts (Figure 1c). After the modification, the emergence of an ordered mesoporous structure with a diameter of 2.5–3.5 nm was observed, instead of the packing pore with a diameter of 1.0–4.0 nm for the HZSM-5 catalyst. The NH_3-temperature programmed desorption profiles of HZSM-5 and Si/PLaHZSM-5 catalysts are shown in Figure 1d. The HZSM-5 catalyst demonstrated weaker and stronger acidic sites, with the desorption peaks centered at 235 and 467 °C, respectively. For the Si/PLaHZSM-5 catalyst, the stronger acidic sites disappeared completely and part of the weaker acidic sites remained and shifted to 196 °C, which could be attributed to the fact that the formation of P hydroxyl (Scheme 2) during the P/La modification decreased the interaction of the silane agent with surface Al atoms in the molecular

Table 1. Performance of the alkylation of toluene with methanol.[a]					
Variable	HZSM-5	Si/PLaHZSM-5			
toluene/methanol ratio [mol]	2:1	0:1	0:1	1:1	2:1
reaction temperature [°C]	420	420	550	420	420
toluene conversion [wt%]	37.48	–	–	38.11	24.19
methanol conversion [wt%]	100.00	85.59	99.77	99.03	99.57
product distribution [wt%]					
C$_1$–C$_5$ hydrocarbons	7.31	89.95	84.26	16.66	11.35
benzene	20.76	0.16	0.61	0.17	0.17
toluene	–	1.11	4.03	–	–
ethylbenzene	0.90	0.34	0.52	0.29	0.21
para-xylene	12.35	5.95	9.60	75.66	82.54
meta-xylene	27.48	0.00	0.05	1.66	1.23
ortho-xylene	11.70	0.03	0.08	1.05	0.83
>C$_9$ hydrocarbons	19.50	2.46	0.84	4.51	3.67
total	100.00	100.00	100.00	100.00	100.00
xylene composition [wt%]					
para	23.97	99.46	98.66	96.54	97.57
meta	53.33	0.00	0.51	2.12	1.45
ortho	22.70	0.54	0.82	1.34	0.98
C$_1$–C$_5$ composition [wt%]					
CH$_4$	3.74	5.69	8.90	2.55	2.75
C$_2$H$_4$	3.50	26.81	22.45	51.77	55.79
C$_2$H$_6$	5.04	0.44	0.55	0.24	0.28
C$_3$H$_6$	2.08	31.56	37.85	32.21	29.83
C$_3$H$_8$	71.46	1.67	2.42	3.16	2.59
C$_4$	11.24	21.33	19.41	8.66	7.41
C$_5$	2.89	12.50	8.43	1.41	1.35
total	100.00	100.00	100.00	100.00	100.00
C$_2$H$_4$ + C$_3$H$_6$	5.58	58.37	60.30	83.98	85.62

[a] Weight hourly space velocity (WHSV) = 2 h^{-1}; atmospheric pressure; time on stream = 10 min.

a gas chromatograph equipped with a flame ionization detector. The gas phase products were collected and analyzed by another gas chromatograph to determine C$_1$–C$_5$ distribution. The reaction results are summarized in Table 1.

When the alkylation of toluene with methanol performed over the HZSM-5 catalyst with a toluene/methanol feed molar ratio of 2:1, toluene conversion and methanol conversion was 37.48 and 100.00%, respectively. The selectivity toward PX among xylene isomers was only 23.97 wt%, which was close to the thermodynamic equilibrium concentration. At the same time, the selectivity toward propane largely formed among C$_1$–C$_5$ hydrocarbons was 71.46 wt%, and an amount of ethylene and propylene was also observed. The results indicated that the secondary isomerization of PX and hydrogen transfer reaction occurred simultaneously in addition to the primary alkylation reaction over the HZSM-5 catalyst.

Over the Si/PLaHZSM-5 catalyst, the proportion of PX among xylene isomers was approximately 96.54 and 97.57 wt% with the toluene/methanol feed molar ratio of 1:1 and 2:1, respectively. If neat methanol was fed (toluene/methanol = 0:1), the selectivity toward PX among xylene isomers was approximately 99.46 wt%. These results indicated that the Si/PLaHZSM-5 catalyst possessed an excellent shape selectivity in both toluene alkylation and methanol-to-aromatics processes.

This observation could be attributed to the fact that ordered mesoporous structure (Figure 1b and f) and narrower average micropore opening (Figure 1c) were favorable for the diffusion of product molecules with the smallest size among xylene isomers and the deactivation of acidic sites (Figure 1d) was conducive to decrease the secondary reactions of product molecules on the external surface, which led to significant contribution to the formation of PX.

In addition, if the toluene/methanol feed molar ratio was 1:1 and 2:1, methanol conversion was more than 99% at 420°C over the Si/PLaHZSM-5 catalyst. However, if neat methanol was fed, methanol conversion was only 85.59% at the same temperature. However, if the temperature was increased to 550°C, methanol conversion could reach 99.71%. These results indicated that methanol conversion increased significantly at lower temperatures with the co-feeding of toluene and methanol.

In the MTH reaction, if neat methanol was fed, the selectivity toward ethylene and propylene among the C$_1$–C$_5$ hydrocarbons was only 58.37 wt% at 420°C and increased to 60.30 wt% at 550°C. However, if toluene and methanol were co-fed in a molar ratio of 1:1 and 2:1, the selectivity toward ethylene and propylene reached 83.98 and 85.62 wt%, which was comparable with the performance of the SAPO-34 catalyst.[17] The selectivity toward ethylene was approximately 55.79 wt% if toluene and methanol were co-fed in a molar ratio of 2:1, which was quite different from the selectivity obtained if only methanol was fed (26.81 wt%) at the same temperature. These results indicated that the presence of toluene favored the production of ethylene and propylene, particularly of ethylene, over the Si/PLaHZSM-5 catalyst.

Therefore, if toluene and methanol were co-fed, high selectivity toward PX among xylene isomers and high conversion of methanol were well maintained and, at the same time, high selectivity toward ethylene and propylene in gas phase products was obtained in methanol transformation over the Si/PLaHZSM-5 catalyst. An interesting observation was that the selectivity toward ethylene increased significantly and was higher than that of propylene.

To identify the reason why the co-feeding of toluene and methanol was conducive to methanol conversion, the performance of the single-pulse reaction was investigated by using different feeding methods: feeding with methanol only and co-feeding with toluene and methanol. The contact time could be altered by changing the bed height and partial pressure of feed components. Methanol conversion as a function of contact time is plotted in Figure 2. The curve slope is used to represent the consumption rate of methanol.[18] The intersection point between the curve and the x axis is the maximum value of contact time when methanol conversion is zero, which is considered as the reaction induction period in methanol transformation. The performance of the single-pulse reaction indicated that methanol conversion increased linearly with
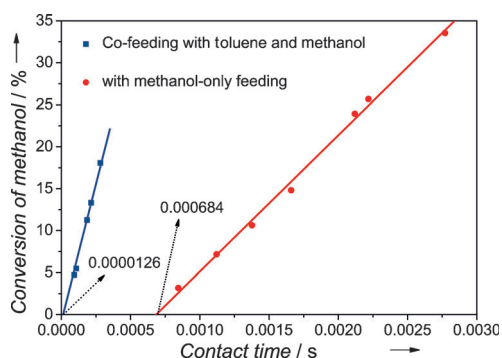
Figure 2. Methanol conversion as a function of contact time over the Si/PLaHZSM-5 catalyst in different feeding methods.

Figure 3. Product distribution as a function of reaction temperature in the TPSR by using different preadsorption methods: a) preadsorption with methanol only and b) preadsorption with toluene and methanol. The insets show clearly the desorption peaks of products when the signal intensity is amplified.

contact time in both feeding methods. With the increase in contact time, the methanol consumption rate remains unchanged. The intersection point is 0.000684 s if the curve for the feeding with methanol only is extended to the x axis, which suggests that the reaction induction period existed in methanol transformation over the Si/PLaHZSM-5 catalyst. However, the intersection point is 0.0000126 s if the curve for the co-feeding with methanol and toluene is extended to the x axis. This result indicated that the reaction induction period in methanol transformation shortened in the presence of toluene. It was also possible that methanol conversion in the MTH process increased in the presence of toluene or as-produced aromatics. This observation was in accordance with the hydrocarbon pool mechanism,[19, 20] in which large aromatics, such as multi-methylbenzene, was considered as the catalytic engine to promote methanol conversion. In the alkylation of toluene with methanol, these lower methylbenzenes that were largely fed (toluene) or produced (xylene) improved methanol transformation correspondingly.

To understand why the co-feeding of toluene and methanol was conducive to selectivity toward ethylene and propylene, the performance of the temperature-programmed surface reaction (TPSR) was investigated by using different preadsorption methods: preadsorption with methanol only and preadsorption with toluene and methanol. Product distribution as a function of reaction temperature in the TPSR is plotted in Figure 3. The products of the TPSR of toluene with methanol were detected as methane, ethylene, and propylene. Owing to the presence of a large amount of toluene covered with the raw material in MS detection, no xylene was detected in the product distribution of the TPSR.

By using the method of preadsorption with methanol only, a weak desorption peak of propylene at 186.9 °C and two desorption peaks of methane at 147.0 and 249.8 °C were observed. A negligible desorption peak of ethylene appeared at 188.4 °C. These results indicated the existence of the reaction induction period in methanol transformation: Methane production was associated with carbon deposition. With the increase in the carbon content up to a certain amount, the reaction induction period ended and light olefins, particularly propylene, were produced quickly. By using the method of preadsorption with toluene and methanol, the desorption temperature of
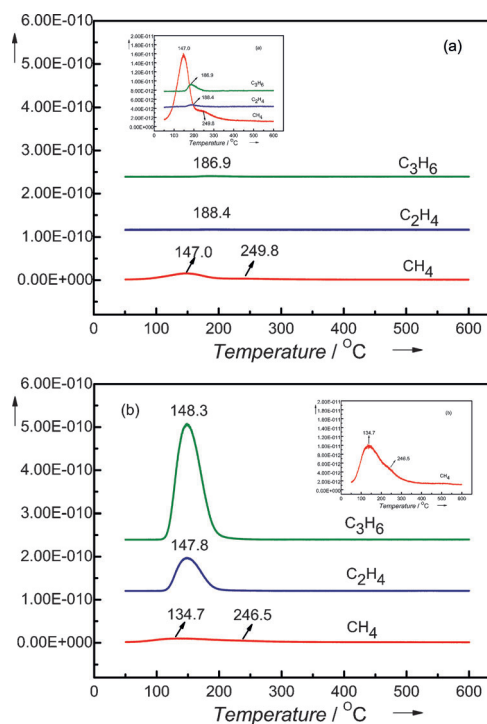
methane was lowered to 134.7 °C, suggesting the shortening of the reaction induction period in the presence of toluene, which was in accordance with the result of the single-pulse reaction (Figure 2). The desorption peaks of ethylene and propylene were observed at 147.8 and 148.3 °C, respectively, which suggested that the formation temperature of ethylene and propylene, particularly of ethylene, decreased in the presence of toluene and methanol co-feed. Considering that the as-produced xylene could also work as the reaction center for ethylene formation,[20, 21] the presence of toluene and xylene was beneficial to the formation of ethylene in methanol transformation, which was in accordance with the result of alkylation of toluene with methanol (Table 1). However, in both preadsorption methods, two desorption peaks of methane were observed at approximately 140 and 250 °C. These results indicated that methane production occurred in two ways: one was associated with the carbon deposition at the initial stage of the reaction and the other was accompanied by the generation of hydrocarbons in methanol transformation.

Coke species were also examined in different feeding methods (feeding with methanol only and co-feeding with toluene and methanol) over the Si/PLaHZSM-5 catalyst. The zeolite frameworks of the used samples were dissolved in a 25% aqueous solution of hydrofluoric acid. After solvent extraction, coke species were identified by using GC–MS and further analyzed quantitatively by using GC, and the results are illustrated in Figure 4. Coke species were mainly composed of methyl-substituted benzene derivatives, naphthalene, dimethylnaph-
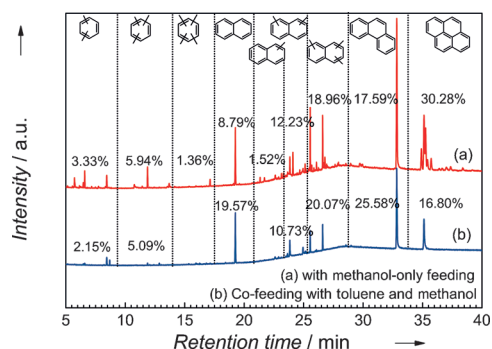
Figure 4. Product distribution and relative composition of coke species over the Si/PLaHZSM-5 catalyst in different feeding methods. Methanol transformation with a toluene/methanol/water (molar ratio) of 2:1:2 for 4 h and a toluene WHSV of 2 h^{-1}. The values in percent denote the relative composition of the corresponding coke species.

thalene, multi-methylnaphthalene, and condensed ring aromatic hydrocarbons such as phenanthrene and pyrene over the Si/PLaHZSM-5 catalyst in both feeding methods. However, less coke was formed and the contents of naphthalene (19.57%) and multi-methyl-substituted derivatives (30.80%) introduce higher intensity in the reaction with toluene and methanol co-feed than do coke species of the reaction with methanol-only feed, in which a larger amount of coke species was detected and the content of polycyclic aromatic hydrocarbons was high (47.87%). These results indicated that coke species were similar in both feeding methods and the formation of the condensed ring aromatic hydrocarbons could be inhibited owing to the replacement of toluene with larger-diameter molecules on the catalyst surface in the co-feeding method. Furthermore, the presence of polycyclic aromatic hydrocarbons in coke species with methanol-only feeding would be conducive to the occurrence of hydrogen transfer reactions, which results in a decrease in the selectivity toward ethylene and propylene.

The reaction of toluene with methanol was further tested for 120 h over the Si/PLaHZSM-5 catalyst, and the reaction results are illustrated in Figure 5. A toluene conversion of greater than 15% and a methanol conversion of greater than 75% were maintained for approximately 120 h. This long-term sta-
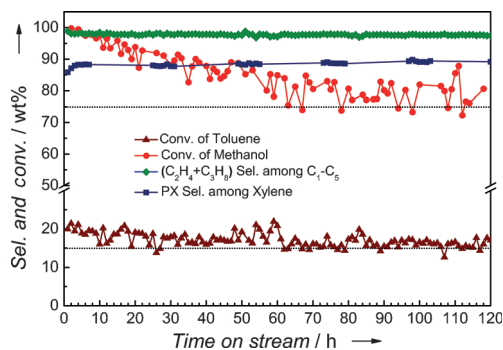
bility could be due to the fact that the reduction in the formation of the condensed ring aromatic hydrocarbons confirmed in the examination of coke species would help retard coke and prolong catalyst life. In addition, greater than 97 wt% selectivity toward PX among xylene isomers and greater than 85 wt% selectivity toward ethylene and propylene among C_1–C_5 hydrocarbons were observed. A life test demonstrated that high activity and selectivity were still well maintained, which confirmed the high hydrothermal stability and sustainable durability of the Si/PLaHZSM-5 catalyst. Hence, the Si/PLaHZSM-5 catalyst not only demonstrated high activity and selectivity in the reaction of toluene with methanol but was also sufficiently stable under practical conditions.

In conclusion, ethylene, propylene, and PX could be produced in one chemical reaction over the Si/PLaHZSM-5 catalyst. The high selectivity toward PX could be well maintained, and light olefins were formed with high efficiency in the transformation of toluene and methanol. A substantial improvement in selectivity toward light olefins, particularly selectivity toward ethylene among C_1–C_5 hydrocarbons, which was different from the classical process of methanol-to-olefin conversion, may stem from the presence of toluene and as-produced xylene. This study gives a potential way of providing two reactants for polyester production in one chemical reaction.

Experimental Section

Figure 5. Lifetime in the reaction of toluene with methanol over the Si/PLaHZSM-5 catalyst. Methanol transformation with a toluene/methanol/water(mol) ratio of 2:1:2 and a toluene WHSV of 2 h^{-1}.

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