A New Catalytic Process for High-Efficiency Synthesis of *p*-xylene by Methylation of Toluene with CH_3Br

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A new catalytic process for p-*xylene synthesis from the methylation of toluene with CH_3Br was proposed. CH_3Br was prepared from the catalytic bromination of natural gas (CH_4), by using H_2O HBr O_2 as mediator over supported Rh catalyst. The methylation conditions were investigated using HZSM-5 or modified HZSM-5 catalyst. Under optimal reaction conditions,* p-*xylene selectivity is up to 93%, and* p-*xylene yield is more than 21% at 673 k over the SiP modified HZSM-5 catalyst. Compared to the processes using MeOH or dimethyl carbonate (DMC) as methylation agent, this new process is very attractive in an economic standpoint since CH_4 is much cheaper than MeOH and DMC. In addition, the process has other advantages, such as mild reaction conditions, simple operation, high-product yield, and so on. It is predicted that the process has good industrial potential for* para-*xylene production.* © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 532–540, 2013

Keywords: bromomethane, p-Xylene, toluene, HZSM-5, methylation

Introduction

p-Xylene is an important aromatic molecule and is used as a raw material for the formation of terephthalic acid for the manufacture of polyester resins and fibers.[1] *p*-Xylene is mainly produced by toluene selective disproportionation,[2–5] adsorptive separation or crystallization from the other xylene isomers. Although these methods produce high-purity *p*-xylene, relatively high cost is required to obtain it in the desired purity. On the other hand, a considerable amount of benzene is produced as a byproduct in toluene selective disproportionation. In the past decades, many researchers have conducted studies on the synthesis of *p*-xylene by selective alkylation of toluene with methanol over various kinds of heterogeneous catalysts, e.g., ZSM-5,[6–8] zeolite X,[9] zeolite Y,[10] zeolite Beta,[11] modernite,[12] ZSM-12/ZSM-5,[13] and silicalite/HZSM-5.[14–16] Although the alkylation of toluene with methanol to prepare *p*-xylene is a promising synthetic method, a relatively high-reaction temperature (ca. 500°C) is needed, resulting in many side reactions and coke deposition on catalysts.[6] Moreover, the selectivity to and yield of *p*-xylene is not good. Very recently, Li et al.[17–18] reported the use of dimethyl carbonate (DMC) as an alkylation agent for the preparation of *p*-xylene from toluene. However, low-catalytic activity and poor *para*-selectivity were observed over the employed MgO/MCM-22 catalyst, and DMC is not cheap compared to methanol or CH_4.

In recent years, we conducted researches on aromatics preparation and natural gas conversion.[19–23] A route (Scheme 1) has been developed for the catalytic conversion of methane using HBr as mediator in the presence of oxygen and H_2O.[19–26] The method involves the conversion of methane into CH_3Br over a suitable catalyst, followed by the catalytic transformation of CH_3Br to higher hydrocarbons and/or other compounds. The steps are conducted at atmospheric pressure, and the HBr is recycled and reused. Because CH_4 is relatively cheap, it is highly desirable to develop a new catalytic process for the use of CH_3Br as an alkylation agent to transfer toluene into *p*-xylene.

In this article, a new process for preparation of *p*-xylene through the alkylation of toluene with CH_3Br is proposed (Scheme 2). In fact, CH_4 acts as indirect alkylation agent because HBr is recycled in the system. We examined different catalysts for this reaction and optimized the reaction conditions. In addition, different characterization techniques (e.g., XRD, SEM, NH_3-TPD, and BET), was employed to disclose the relationship between structure and surface properties of the catalysts as well as the critical factors influencing the *p*-xylene selectivity.

Experimental

Catalysts preparation

HZSM-5 zeolite with a Si/Al ratio of 50 which was synthesized by hydrothermal method was used as parent

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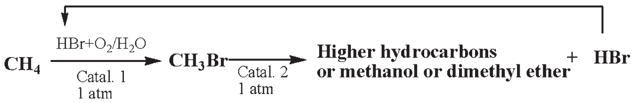


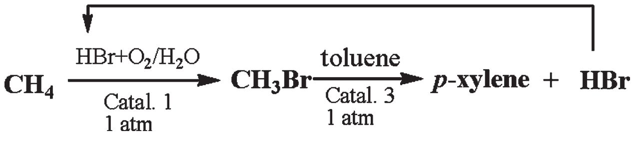
Scheme 1. The route for catalytic conversion of methane using HBr as mediator in the presence of oxygen and H_2O.

material. The molar ratio of the synthesis solution was 100 SiO_2:1 Al_2O_3:20 TPAOH:20 NaOH:4800 H_2O; and tetraethyl orthosilicate and aluminum nitrate were used as silicon and alumina source, respectively. The synthesis solution was mixed and stirred for 60 min at room temperature and then poured into a Teflon-lined stainless-steel autoclave for hydrothermal treatment at 453 K for 24 h. The solid product was separated by centrifugation, washed several times with distilled water and ethanol, dried overnight at 383 K, and calcined in air at 873 K for 7 h. Finally, NH_4-ZSM-5 was obtained by ion exchange twice with 1 M ammonium nitrate solution at 353 K for 3 h. Then the zeolite was washed thoroughly with deionized water, followed by drying at 383 K, and calcining at 813 K for 4 h sequentially to form H—ZSM-5 zeolite.

Most of the modified samples were prepared by the impregnation method at ambient temperature for 4 h, followed by drying at 353 K, and then calcining for 4 h at 813 K. The Si/HZSM-5 catalysts were obtained by impregnating HZSM-5 samples with methyl silicon oil dissolved in cyclohexane.

Catalyst characterization

The phase structure of the catalysts were characterized by powder X-ray diffraction (XRD) analysis conducted on a Rigaku automatic diffractometer (Rigaku D-MAX), with monochromatized Cu K_α radiation ($\lambda = 0.15406$ nm) at a setting of 40 kV and 80 mA. BET surface area, pore volume and pore size were measured by using a Micrometrics 201°C instrument. Scanning electron microscopy (SEM) was employed to study the morphology and particle size of HZSM-5 zeolite. Temperature-programmed desorption of ammonia (NH_3-TPD) experiments were carried out on a Micrometrics 2920 apparatus to analyze the acid property of the catalysts. As described elsewhere,[27] the acidity of the external surface of the catalyst was measured by cracking 1,3,5-triisopropylbenzene (1,3,5-TIPB) molecules which are too large to enter into the pores of HZSM-5 zeolite. The procedure is: the catalysts (0.5 g) were installed in quartz glass tube, and activated at 673 K for 1 h in a flow of nitrogen before the introduction of 1,3,5-TIPB ($WHSV_{1,3,5\text{-TIP}}B = 1$ h^{-1}) into the reactor tube at 623 K. The cracking products were propylene, benzene, toluene, ethylbenzene, xylene, trimethylbenzene, and so on. The external surface acidity was evaluated based on the conversion of 1,3,5-TIPB, i.e., (1 - $TIPB_{unreacted}$/sum of products including benzene ring + $TIPB_{unreacted}$) × 100%.[28]



Scheme 2. Process for preparation of *p*-xylene from the alkylation of toluene with CH_3Br.

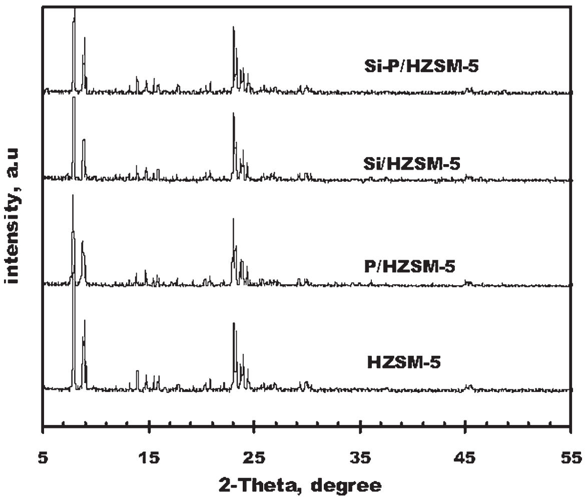


Figure 1. XRD patterns of unmodified and modified catalysts.

Catalytic evaluation

The alkylation of toluene with CH_3Br was carried out over a continuous fixed-bed quartz reactor, the experimental setup is similar to that reported previously.[23] CH_3Br was prepared from the catalytic bromination of natural gas (CH_4) by using H_2O + HBr + O_2 as mediator over supported Rh catalyst, as described elsewhere.[29] The synthesized CH_3Br gas was separated and carried by N_2 into the methylation reactor, which was filled with HZSM-5 or its modified samples. Substrate of toluene was fed by a syringe pump. The liquid products in the second hour were collected in an ice-water condenser and qualitatively analyzed on a GC/MS (6890N/5973N) using an Agilent HP-5MS capillary column (30 m × 0.45 mm × 0.8 μm). For quantitative determination, the collected liquid products were analyzed on an Agilent 7820A GC with FID and Agilent AB—FFAP capillary column (30 m × 0.25 mm × 0.25 μm). The conversion of CH_3Br and gaseous products were analyzed on an Agilent 6890N GC with TCD, and Agilent GS—GASPRO capillary column (30 m × 0.32 mm × 0.25 μm).

Results and Discussion

Catalyst characterization

The XRD patterns of different catalysts are shown in Figure 1. It can be seen that there are no characteristic peaks related to the corresponding oxides (P_2O_5, SiO_2) detected over the modified samples, suggesting that the loaded oxides are highly dispersed on the surface of HZSM-5. In addition, there is no change of structure and relative crystallinity of HZSM-5 after the modification treatment.

The morphology and crystal size of the synthesized HZSM-5 is shown in Figure 2. The SEM image shows that the crystals are hexagonal cylindrical in shape (average size: 0.6 × 0.9 × 1.5 μm).

The NH_3-TPD curves of unmodified and modified zeolites are shown in Figures 3 and 4; the acid amount and strength distribution of each catalyst are depicted in Table 1. It can be seen from Figure 3 that there are two desorption peaks detected over HZSM-5, one at high temperature (633 K), and the other at low temperature (433 K), attributable to strong and weak acid sites,[30] respectively. Over the phosphoric acid modified HZSM-5 catalysts, one can see that

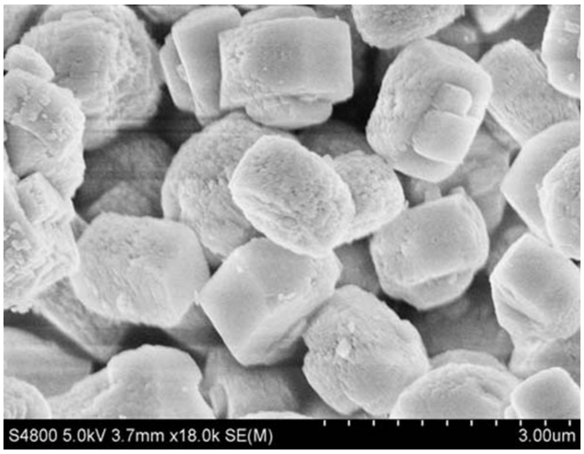


Figure 2. SEM images of HZSM-5 crystals.

with the increase of P_2O_5 loading, there is rapid decrease in the amount of acid sites, especially the strong ones. At a P_2O_5 loading of 9 wt %, there is almost complete elimination of strong acid sites. Similar results were observed when HZSM-5 zeolite was modified with methyl silicon oil (depicted in Figure 4). However, the total amount of weak acid sites after silicon modification is more than that after phosphoric acid modification. It is plausible that the molecular diameter of methyl silicon oil is so much larger that Si deposition occurs only on the external surface of HZSM-5 zeolite, and the internal acid sites of HZSM-5 zeolite are not covered.

The changes of specific surface area and pore volume of HZSM-5 zeolite after modification are listed in Table 2. It is clear that HZSM-5 and Si/HZSM-5 are similar in micropores volume. It can be deduced that because the molecules of methyl silicon oil are larger than the pore size of HZSM-5 zeolite, they could not penetrate into the channels of HZSM-5. However, because phosphoric acid can enter into the channels of HZSM-5, modification of zeolite with phosphoric acid leads to a decline of pore volume (from 0.149 to 0.127 cm^3), and surface area (from 385.9 to 373.6 m^2/g).

Catalyst screening

In recent decades, toluene methylation to prepare *p*-xylene is considered to be a promising process and has been studied extensively.[14–18,31–38] ZSM-5 zeolite, owing to its unique structure possessing pores of intermediate size (0.5–0.6 nm), has been used extensively as shape-selective catalyst, and lots of measures have been carried out to improve *para*-selectivity, such as modification with metallic[31–34] or nonmetallic agents,[35–36] surface silanation,[37–38] use of ZSM-5/silicalite composites,[14–16] and by optimization of the process variables.[34,36] In this study, we chose HZSM-5 zeolite as parent catalyst and screen the modifiers that were reported in toluene methylation with methanol.

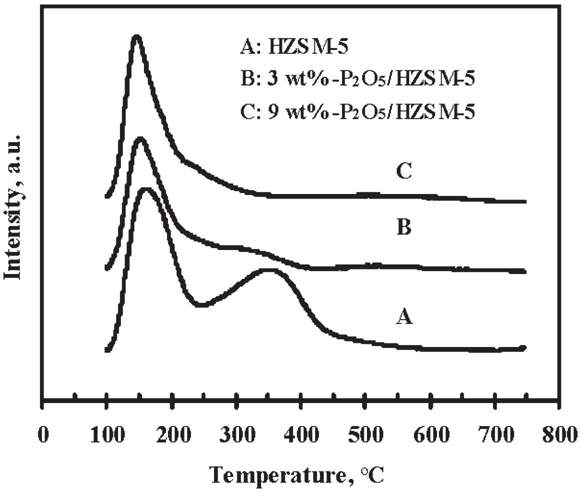


Figure 3. NH_3-TPD curves of HZSM-5, 3 wt % P_2O_5/HZSM-5 and 9 wt % P_2O_5/HZSM-5.

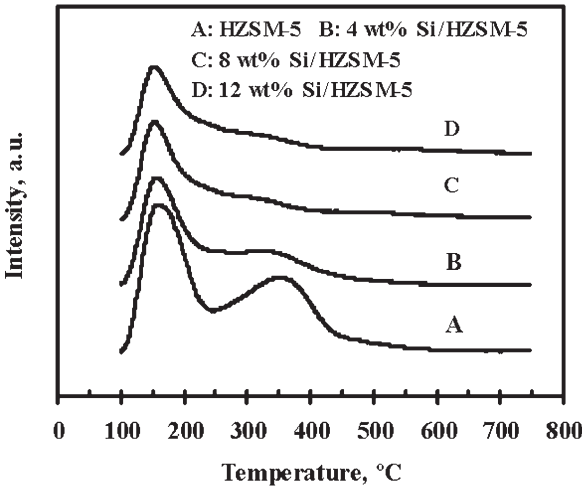


Figure 4. NH_3-TPD curves of HZSM-5, 4 wt % Si/HZSM-5, 8 wt % Si/HZSM-5 and 12 wt % Si/HZSM-5.

Table 3 summarizes the conversion of toluene, *p*-xylene yield and *para*-xylene selectivity detected over a range of modified catalysts. Compared to unmodified HZSM-5, all the modified HZSM-5 catalysts give a higher *para*-selectivity at the cost of decreasing the conversion of toluene. In terms of *para*-selectivity, P_2O_5, SiO_2, MgO, La_2O_3, and Sb_2O_3 are good promoters, especially for P_2O_5 which is well-known as a good modifier for toluene disproportionation and methylation.[35] However, with the loading of MgO, La_2O_3, or Sb_2O_3, there is significant decrease in toluene conversion. It is clear that among the catalysts tested, P/HZSM-5 shows the highest *p*-xylene selectivity (up to 83.5%). The Si/HZSM-5 catalyst is somewhat less-selectivity (51.7% to *p*-xylene), but gives a higher *p*-xylene yield (20.6%).

Effect of methyl silicon oil modification

Surface silanation is an effective method to enhance *para*-selectivity in toluene methylation (using CH_3OH as methylating agent) and disproportionation.[39] Table 4 shows the effects of methyl silicon oil content on the activity and

Table 1. Acidity of HZSM-5 and its Modified Samples

Catalysts	Total amount of acid sites	Weak acid sites (mmol/g)	p (%)	Strong acid sites (mmol/g)	p (%)
HZSM-5	0.945	0.473	50.1	0.472	49.9
4 wt% Si/HZSM-5	0.568	0.347	61.1	0.221	38.9
8 wt% Si/HZSM-5	0.507	0.393	77.5	0.114	22.5
12 wt% Si/HZSM-5	0.485	0.426	87.8	0.059	12.2
3 wt% P_2O_5/HZSM-5	0.448	0.417	93.1	0.031	6.9
9 wt% P_2O_5/HZSM-5	0.434	0.431	99.3	0.03	0.7

p (%) stands for site amount in percentage.

Table 2. Specific Surface Area and Pore Volume of Different Catalysts

Catalyst	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)
HZSM-5	385.9	0.213	0.149
Si/HZSM-5[a]	391.9	0.215	0.149
P/HZSM-5[b]	373.6	0.190	0.127

[a]methyl silicon oil content is 12 wt %,
[b]phosphorus pentoxide content is 9 wt %.

para-selectivity in the methylation reaction of toluene with CH_3Br. One can see that the conversion of toluene decreases with the rise of methyl silicon oil loading, and with methyl silicon oil content exceeding 12 wt %, *para*-selectivity stabilizes. From the NH_3-TPD results of the Si/HZSM-5 catalysts, it is clear that with the rise of methyl silicon oil content there is almost proportional reduction in the amount of acid sites. The strong acid sites on the external surface and at the pore mouths are completely eliminated when the content of methyl silicon oil reaches 12 wt %. Because it is impossible for methyl silicon oil to penetrate into the channels of HZSM-5 zeolite, the acid sites located on the internal surface are not altered and there are still strong acid sites after the modification. We, hence, deduce that the selectivity to *p*-xylene depends on the weak acid sites, and the strong acid sites are favorable for the isomerization of *p*-xylene.

Effect of phosphorus modification

P_2O_5 has been regarded to be an effective modifier for the reaction of toluene methylation with methanol.[35] We modified HZSM-5 zeolite with phosphoric acid and studied the effect of P_2O_5 content on catalytic reactivity over the P/HZSM-5 catalyst. The content of P_2O_5 was varied from 3 to 9 wt %, and the evaluation results are depicted in Table 5. With the increase of P_2O_5 loading, toluene conversion decreases from 22.0 to 5.4%, and *para*-selectivity increases from 76.7 to nearly 100%. Obviously, when HZSM-5 was modified by P_2O_5 there was a significant rise of *para*-selectivity. The results of NH_3-TPD experiments show that the amount of acid sites decreases with an increase of P_2O_5 loading. It is well-known that toluene methylation is a typical acid-catalyzed Friedel-Crafts reaction. Therefore, it is easy to explain why the activity of P/HZSM-5 catalysts decreases with rise of P_2O_5 content. We know that the dimension of H_3PO_4 is smaller than the pore size of HZSM-5, so the loaded H_3PO_4 distributed on the outer surface as well as inside the channels, altering the entire acidity of HZSM-5. As stated before, about 100% *para*-selectivity is observed when strong acid sites are almost eliminated completely at a P_2O_5 content of 9 wt %. It is known that at such P_2O_5 content, there is no change in terms of micropores volume and most probable pore size (shown in Table 5). Therefore, the experimental results further confirm that the enhanced *para*-selectivity in the reaction of toluene with CH_3Br is mainly due to the elimination of strong acid sites.

The cracking of 1,3,5-TIPB is a suitable probe reaction for determining the activities of external surface of HZSM-5 zeolite. Because a 1,3,5-TIPB molecule is too large to enter into the zeolite pores, the cracking of 1,3,5-TIPB takes place on the external surface. Consequently, the activity of catalysts for the cracking of 1,3,5-TIPB corresponds to the number of acid sites on the external. Figure 5 shows the effect of phosphoric acid and methyl silicon oil modification on cracking 1,3,5-TIPB. It is clear that the external surface acid sites are completely inactivated because there is nearly no 1,3,5-TIPB cracking when methyl silicon oil content is 12 wt %. However, the conversion of 1,3,5-TIPB is 2.1% over 9 wt % P_2O_5/HZSM-5 catalyst, indicating that the acid sites on the external surface are not completely inactivated.

Van Vu et al.[16] studied toluene methylation with methanol over ZSM-5/silicalite composites and suggested that the high *para*-selectivity is due to the removal of the acid sites on the external surface by silicalite layer and the suppression of *p*-xylene isomerization. In this study, however, the *para*-selectivity is not improved to a satisfactory extent when the acid sites on the external surface are removed by modification with methyl silicon oil; the results demonstrated that the *para*-selectivity mainly depends on the nature rather than on the distribution of the acid sites.

As stated before, high *para*-selectivity but low activity was observed over P/HZSM-5, whereas high activity but low *para*-selectivity could be obtained over Si/HZSM-5. Satisfactory results cannot be obtained by modification of HZSM-5 zeolite with H_3PO_4 or methyl silicon oil only. To develop high activity and high *para*-selectivity catalyst, combinational modification was carried out using phosphoric acid and methyl silicon oil. The content of methyl silicon oil and P_2O_5 were 8 and 3 wt %, respectively. It was observed (Figure 6) that Si—P/HZSM-5 performed better (93.1% *para*-selectivity, 27.7% toluene conversion) than 3 wt % P_2O_5/HZSM-5 or 8 wt % Si/HZSM-5 under equal reaction conditions.

Table 3. Toluene Conversion, *p*-xylene Yield and Selectivity over Different MO/HZSM-5 Catalysts

Catalysts	*X*(Toluene)%	*Y*(*p*-Xylene)%	Xylene fraction, %		
			p-Xylene	*m*-Xylene	*o*-Xylene
HZSM-5	63	10.0	24.3	53.2	22.5
P/HZSM-5	18.6	13.1	85.3	9.5	5.2
B/HZSM-5	41.0	9.0	30.8	49.6	19.6
Si/HZSM-5	56.5	20.6	51.7	33.9	14.4
Mg/HZSM-5	23.5	8.7	54.6	19.0	26.4
Ca/HZSM-5	18.9	5.7	37.8	46.9	15.3
Al/HZSM-5	53.0	12.7	33.7	41.9	17.4
Zn/HZSM-5	56.7	9.5	26.5	51.3	20.2
La/HZSM-5	43.3	13.9	54.7	29.2	17.1
Pb/HZSM-5	55.2	14.7	39.4	42.0	18.6
Fe/HZM-5	41.6	13.3	40.5	41.6	18.9
Sb/HZSM-5	38.5	16.0	57.9	28.3	13.8
Bi/HZSM-5	54.6	12.7	28.4	51.5	20.1

Reaction conditions: $T = 673$ K, $WHSV_{toluene} = 1.5\ h^{-1}$, $n(CH_3Br):n(toluene) = 2:1$, the oxide content is 5 wt %, N_2 flow 10 mL/min.

Table 4. The Effect of Methyl Silicon Oil Content on Toluene Conversion and Products Distribution

Catalysts	0 wt%	4 wt%	8 wt%	12 wt%	16 wt%
Toluene Conv.,%	63	56.5	53.3	46.4	38.2
CH_3Br Conv.,%	90.1	78.4	71.7	63.2	54.6
Product composition, %					
Benzene	3.7	0.6	0.4	0.2	0.1
Ethyl benzene	0.2	0.2	0.2	0.1	0
p-Xylene	10.0	20.6	23.4	22.7	19.7
m-Xylene	21.9	13.5	10.1	6.3	4.7
o-Xylene	9.3	5.8	4.9	4.3	3.8
Trimethylbenzenes	13.5	13.4	12.2	10.8	8.4
C_{10+}	4.5	2.4	2.1	2.0	1.5
Xylene fraction, %					
p-Xylene	24.3	51.7	60.9	68.1	69.8
m-Xylene	53.2	33.9	26.4	19.0	16.7
o-Xylene	22.5	14.4	12.7	12.9	13.5

Reaction conditions: T = 673 K, $WHSV_{toluene}$ = 1.5 h^{-1}, $n(CH_3Br)$:n(toluene) = 2:1, N_2 flow 10 mL/min.

Effect of Reaction Conditions

Effect of reaction temperature

Toluene methylation with CH_3Br was carried out over Si—P/HZSM-5 catalysts in the 643–733 K range. The CH_3Br/toluene molar ratio was fixed at 2. As shown in Table 6, the conversion of toluene increases with the rise of reaction temperature, whereas *para*-selectivity changes significantly and irregularly between 643 and 733 K, resulting in a maximum of *p*-xylene yield at about 673 K. However, toluene conversion and *p*-xylene yield decrease with further rise of temperature. The conversion of toluene in the methylation reaction may be related to CH_3Br conversion, toluene disproportionation and catalyst deactivation. It was observed that CH_3Br conversion decreases at high temperature (Table 6), implying less participation of CH_3Br in toluene methylation, and, hence, lower conversion of toluene. In addition, the content of benzene increases with the rise of temperature (Table 6), indicating that high temperature is favorable for toluene disproportionation. Catalyst deactivation will lead to the decline of toluene conversion, and coke deposition would narrow the channels and pore mouths of the catalysts, consequently, enhancing *p*-xylene diffusion and improving *para*-selectivity. However, the *para*-selectivity does not increase, but reduces at high-reaction temperature. So, it is speculated that the decrease of toluene conversion at high temperature is mainly due to the conversion of CH_3Br and toluene disproportionation rather than to catalyst deactivation. When studied the alkylation of toluene with methanol over H_3PO_4/ZSM-5, Ghiaci et al.[35] observed *para*-selectivity decrease at high temperature but provided no explanation. The same phenomenon was observed in this study, we deduced that the decrease of *para*-selectivity at high temperature is due to *p*-xylene isomerization.

Table 5. Effect of P_2O_5 Content on Toluene Conversion and Products Distribution

Catalysts	0 wt%	3 wt%	6 wt%	9 wt%
Toluene Conv., %	63.1	22.0	13.1	5.4
CH_3Br Conv., %	90.1	45.0	23.9	14.4
Product composition, %				
Benzene	3.7	0.4	0.3	0.1
Ethyl benzene	0.2	0.1	0	0
p-Xylene	10.0	14.4	10.6	5.0
m-Xylene	21.9	3.2	0.7	0.1
o-Xylene	9.3	1.2	0.3	0.
Trimethylbenzenes	13.5	1.7	1.0	0.3
C_{10+}	4.5	1.0	0.2	0
Xylene fraction, %				
p-Xylene	24.3	76.7	91.9	98
m-Xylene	53.2	16.7	5.9	2
o-Xylene	22.5	6.6	2.2	0

Reaction conditions: T = 673 K, $WHSV_{toluene}$ = 1.5 h^{-1}, $n(CH_3Br)$:n(toluene) = 2:1, N_2 flow 10 mL/min.

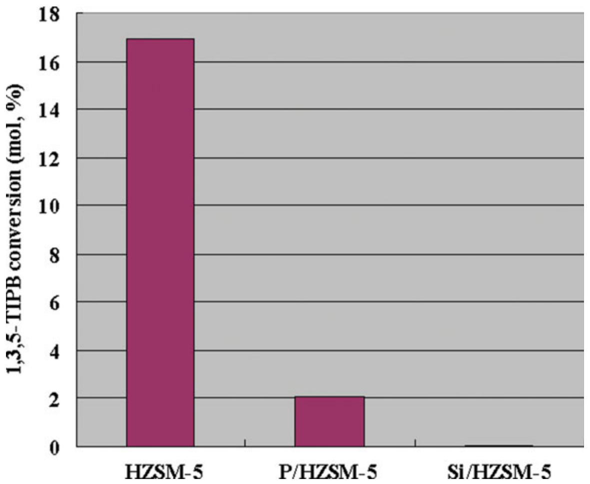


Figure 5. Conversion of 1,3,5-TIPB over HZSM-5, 9 wt % P_2O_5/HZSM-5 and 12 wt % Si/HZSM-5 catalysts.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of WHSH$_{toluene}$

The effect of toluene weight hourly space velocity ($WHSV_{toluene}$) on toluene conversion and *para*-xylene selectivity was studied at 673 K, with the feed ratio of CH_3Br:toluene = 2:1 over Si—P/HZSM-5 catalyst. The results

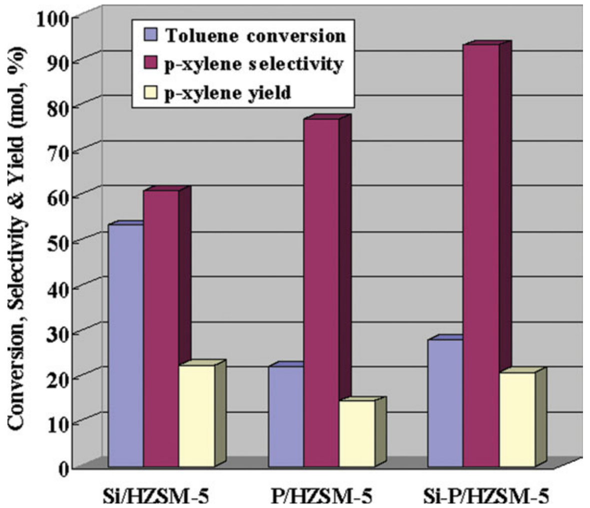


Figure 6. Catalytic performance comparison of P/HZSM-5, Si/HZSM-5 and Si—P/HZSM-5 (reaction conditions: $n(CH_3Br)$:n(toluene) = 2:1, $WHSV_{toluene}$ = 1.5 h^{-1}, T = 673 K, N_2 flow 10 mL/min).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 6. Effect of Temperature on the Reaction of Toluene Methylation with CH_3Br

Temperature (K)	643	673	703	733
Conversion of toluene (%)	25.7	27.7	35.6	30.9
Conversion of CH_3Br (%)	47.9	75.6	57.3	43.2
Product composition (%)				
Benzene	0.1	0.2	0.6	1.0
Ethyl benzene	0.1	0.1	0.2	0.1
xylenes	19.9	23.1	28.8	25.5
Trimethyl benzenes	4.4	3.5	4.8	2.8
C_{10+}	1.2	0.8	1.0	1.5
Fraction of xylenes (%)				
p-xylene	78.7	93.1	74.2	72.1
m-xylene	15.0	5.1	18.7	20.6
o-xylene	6.3	1.8	7.1	7.3

Reaction conditions: $WHSV_{toluene} = 2\ h^{-1}$, $n(CH_3Br):n(toluene) = 2:1$, N_2 flow 10 mL/min.

obtained are summarized in Figure 7. It is clear that the conversion of toluene decreases from 44% to 16.9% when the WHSV of toluene increases from 1 to 3 h^{-1}, and the selectivity to *p*-xylene increases with the rise of toluene WHSV from 61.5% to 99.5%. Ghiaci et al.[35] and Breen et al.[36] observed the same phenomena in the methylation of toluene with methanol. As $WHSV_{toluene}$ increases, the contact time between toluene and catalysts declines. It is plausible that a large number of toluene and CH_3Br molecules passed through the reactor without actually contacting the active sites of the catalysts, resulting in low toluene and CH_3Br conversions. On the other hand, there is fast diffusion of *p*-Xylene out of the catalysts, and *p*-Xylene isomerization over strong acid sites is, hence, limited (leading to the increase of *para*-selectivity).

Effect of feed molar ratio

The effect of varying the CH_3Br/toluene molar ratio from 0.5 to 3 was studied over Si—P/HZSM-5 at 673 K and at toluene space velocity = 2 h^{-1}. The results are depicted in Figure 8. One can see that with the CH_3Br/toluene increases from 0.5 to 3, the conversion of toluene declines from 34.7% to 15.5% and *para*-selectivity increases from 67.1% to 98.6%, whereas *p*-xylene yield reaches a maximum (21.5%) at CH_3Br/toluene = 2. The decline of toluene conversion can be explained by the fact that the active sites (especially the strong acid sites) are mostly occupied by the redundant CH_3Br, and only a small amount of toluene can be activated over the catalyst. Although with increase of CH_3Br/toluene molar ratio, there is reduction in CH_3Br conversion (shown in Figure 8), there is however increase in terms of total CH_3Br conversion. Our previous study[40] demonstrated that CH_3Br conversion requires moderate surface acidity over HZSM-5. Therefore, with increase of CH_3Br/toluene molar ratio, more strong acid sites on Si—P/HZSM-5 would be involved in CH_3Br activation, and there is relatively less participation of strong acid sites in *p*-xylene isomerization. The result is enhancement in *para*-selectivity.

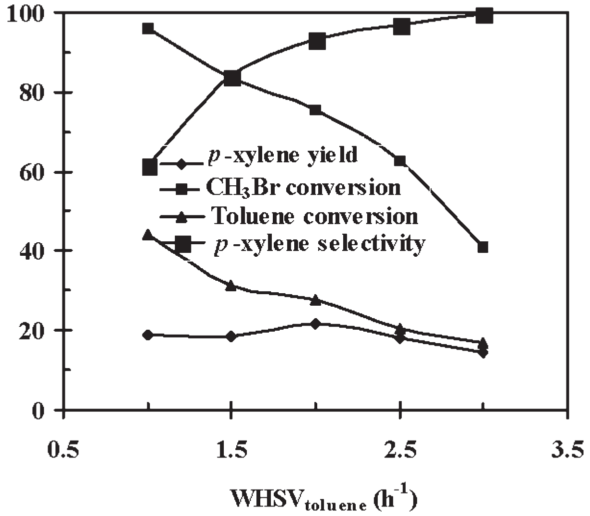


Figure 7. Effect of reaction temperature on the performance of Si—P/HZSM-5 catalyst (Reaction conditions: $n(CH_3Br):n(toluene) = 2:1$, $WHSV_{toluene} = 2\ h^{-1}$, N_2 flow 10 mL/min).

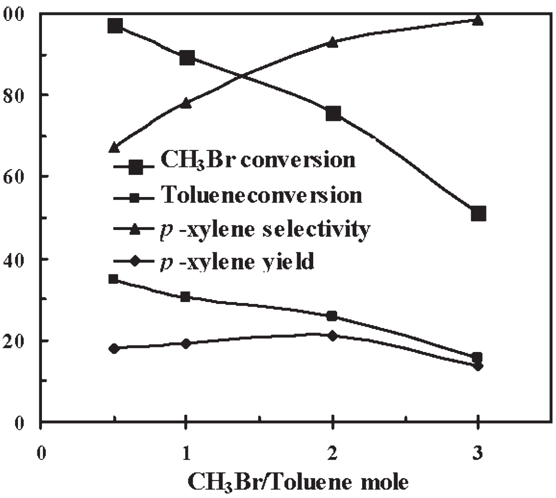


Figure 8. Effect of $n(CH_3Br):n(toluene)$ on the performance of Si—P/HZSM-5 catalyst (Reaction conditions: $T = 673$ K, $WHSV_{toluene} = 2\ h^{-1}$, N_2 flow 10 mL/min).

Effect of time on stream

A time on stream study was carried out over Si—P/HZSM-5 under optimal conditions (673 K, $WHSV_{toluene} = 2\ h^{-1}$, $n(CH_3Br):n(toluene) = 2:1$). As shown in Figure 9, there is

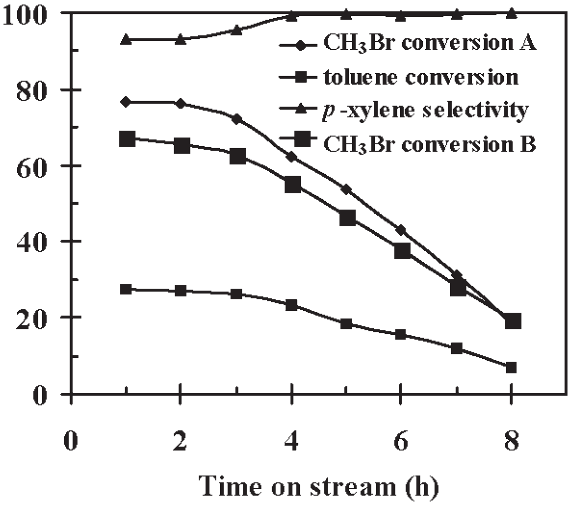


Figure 9. Time on stream of toluene methylation and CH_3Br catalytic conversion (reaction conditions: $T = 673$ K, $WHSV_{toluene} = 2\ h^{-1}$, $WHSV_{CH3B}r = 4.1\ h^{-1}$, N_2 flow 10 mL/min).

Table 7. Products Distribution in CH_3Br Catalytic Conversion over Si—P/HZSM-5

		liquid phase products, %					gas phase products, %						Xylene fraction, %		
X, %	Y, %	C_6	C_7	C_8	C_9	C_{10+}	C_2	$C_{2=}$	C_3	$C_{3=}$	C_4	$C_{4=}$	*p*-xylene	*m*-xylene	*o*-xylene
64.6	21.3	2.2	23.4	57.5	5.9	11.0	31.8	9.5	26.5	1.1	37.3	3.8	90.1	6.5	3.4

Reaction conditions: $T = 673$ K, $WHSV_{CH3Br} = 4.1\ h^{-1}$, N_2 flow 10 mL/min.
X: CH_3Br conversion, Y: Aromatics yield.

Table 8. Products Distribution in Toluene Methylation with CH_3Br over Si—P/HZSM-5

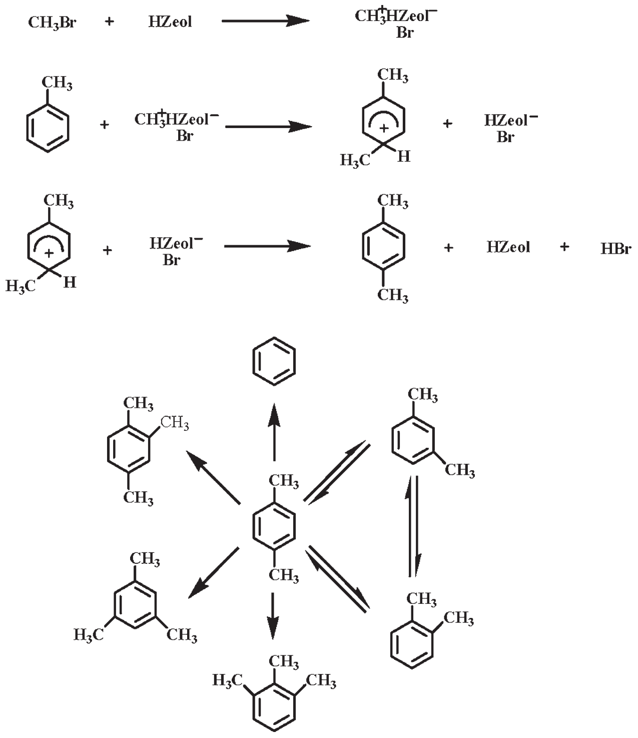
liquid phase products, %					gas phase products, %					
C_6	C_7	C_8	C_9	C_{10+}	C_2	$C_{2=}$	C_3	$C_{3=}$	C_4	$C_{4=}$
0.7	0.5	83.5	12.6	2.7	23.8	7.5	2.6	2.3	60.8	3.0

Reaction conditions: $T = 673$ K, $WHSV_{toluene} = 2\ h^{-1}$, $n(CH_3Br):n(toluene) = 2:1$, N_2 flow 10 mL/min.

almost no change in both CH_3Br (marked as CH_3Br conversion A) and toluene conversions in the first 3 h (respectively staying at about 26% and 75%). When the reaction time is further extended, CH_3Br conversion decreases significantly (from 75% to 18%), and toluene conversion decreases from 26% to 7%, whereas the *para*-selectivity increases to an admirable value (>99%) and remains rather stable. It is clear that the decline rate of CH_3Br conversion is much larger than that of toluene. As discussed before, the conversion of toluene over Si—P/HZSM-5 catalyst is mainly due to the conversion of CH_3Br. To disclose the relationship between CH_3Br conversion and the activity (toluene conversion) of Si—P/HZSM-5, we investigated the catalytic conversion of CH_3Br separately (marked as CH_3Br conversion B) over Si—P/HZSM-5. The conversion and products (liquid products were collected in the first 2 h) distribution are depicted in Figure 9 and Table 7, respectively. One can see that the change of CH_3Br conversion in the catalytic reaction is similar to that in toluene methylation. In both reactions the conversion of CH_3Br is stable in the first 3 h, and declines significantly in the next 5 h. The results of CH_3Br conversion, aromatics yield as well as products distribution in the liquid and gas phases in CH_3Br catalytic conversion over Si—P/HZSM-5 are somewhat different from those reported before.[23,40] In addition, the distribution of gas phase products in CH_3Br catalytic conversion is also different from those (shown in Table 8) in the reaction of toluene methylation with CH_3Br. The different results may be attributed to the variation of surface acidity across the catalysts. We found that CH_3Br conversion needs an appropriate ratio of strong and weak acid sites.[40] Based on the overall results of these two reactions (toluene methylation and CH_3Br catalytic conversion in this study), one comes to the awareness that the conversion of CH_3Br has much to do with the catalytic activity (toluene conversion) of the catalyst. We deduce that CH_3Br is first activated on the strong acid sites, yielding intermediates such as CH_3^+ or CH_2, then the intermediates move to the weak acid sites and undergo methylation, oligomerization and coking reactions. The formed coke covers the active sites, especially the strong acid sites, and reduces the conversion of toluene and CH_3Br. On the other hand, the blocking of strong acid sites by coke improves *para*-selectivity.

The possible reaction mechanism

Kaeding et al.[41] studied the reaction of toluene methylation with methanol over modified HZSM-5 catalyst and proposed a mechanism: first, methanol or methyl ether (formed by methanol dehydration over modified HZSM-5 catalyst) adsorbed on the acid sites of catalyst and formed the corresponding oxonium ion. Then the methyl group transferred to the aromatic ring and a proton transferred back to the catalyst site. According to the results of this study and the mechanism reported by Kaeding et al. we propose a possible mechanism of toluene methylation with CH_3Br over Si—P/HZSM-5 (Scheme 3). First, CH_3Br chemisorbed on the strong acid sites and yields methyl cations. Then the electrophilic agents attack toluene to form *p*-xylene on the weak acid sites. Hereafter, the isomerization of *p*-xylene takes place on the strong acid sites and a mixture of all xylene (*p*-xylene, *m*-xylene and *o*-xylene) are produced. With a sufficient supply of CH_3Br, xylene further methylates to produce tri- and tetramethylbenzenes. At the same time, toluene disproportionation undergoes over the Brønted acid sites of the catalysts. According to the results shown in Table 6, the conversion of CH_3Br (75.6%) is much higher than that of toluene (27.7%) under optimal reaction conditions, indicating that there is considerable CH_3Br depletion due to oligomerization and/or coking reactions. As shown in Table 7, toluene (23.4%), and xylenes (57.5%), are dominant liquid-phase



Scheme 3. Plausible reaction mechanism over Si—P/HZSM-5 catalyst.

products in CH_3Br oligomerization, and the gas-phase products are mainly C_2 (41.3%) and C_4 (41.4%). The *para*-selectivity in CH_3Br catalytic conversion (90.1%) is close to that in toluene methylation (93.1%). In view of the product distribution, we consider that the mechanism of side reactions is similar to those reported elsewhere,[23,40] caused only by CH_3Br in toluene methylation.

Conclusion

A new catalytic process for *p*-xylene synthesis from toluene methylation with CH_3Br was found feasible. The process has advantages such as mild reaction conditions, simple operation, high-product yield, and so on. It was found that Si—P/HZSM-5 is an excellent catalyst for selective formation of *p*-xylene in toluene methylation with CH_3Br. The catalyst is highly active and selective and the yield of *p*-xylene is up to 21%. It was found that toluene conversion depends on the concentration of total acid sites, whereas the *para*-selectivity depends on the relative ratio of strong to weak acid sites: decline in strong acid sites would mean better *para*-selectivity. Furthermore, the isomerization of *p*-xylene to other xylene isomers does not depend on whether the strong acid sites are inside or on the external surface of the zeolite, and elimination of strong acid sites in either location increases *para*-selectivity. The deactivation of Si—P/HZSM-5 in toluene methylation with CH_3Br is mainly due to CH_3Br oligomerization and coke formation.

Acknowledgments

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