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Kinetics of Toluene Methylation over ZSM-5 Catalyst in a Riser Simulator

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Toluene methylation has been studied over fresh and precoked ZSM-5 based catalyst in a riser simulator, which closely mimics the operation of commercial fluidized-bed reactors. The study was carried out at 375, 400, 425, and 450 °C for reaction times of 3, 5, 7, 10, 13, and 15 s. Toluene conversion was found to increase with reaction temperature and time for both forms of the catalyst. Maximum toluene conversion of 16.81% was obtained over the fresh catalyst at 450 °C. The ratio of *para-/ortho*-xylene (P/O) in the reaction products was much higher than the equilibrium value for all reaction conditions with P/O ratios as high as 3.5–6 times the equilibrium value achieved. For the fresh catalyst, a maximum P/O ratio of 5.6 was attained at 400 °C, while the minimum value of 3.17 was observed at 450 °C. Partial deactivation of the fresh catalyst with coke deposit from 1,3,5-triisopropyl benzene (TIBP) was found to have a significant effect on the product distribution, as reflected by increased P/O and xylene yield/TMB yield ratios. For the same toluene conversion, P/O ratios for the precoked catalyst were found to be 25–30% higher than those of the fresh catalyst. Similarly, the xylene yield/TMB yield ratios for the precoked catalyst were found to be 25–36% higher than those of the fresh catalyst. The experimental results were modeled over the fresh catalyst using the time-on-stream model, and the activation energy of toluene methylation was found to be ~67.79 kJ/mol.

1. Introduction

The increasing application of xylene as an intermediate for the production of a wide range of useful materials like synthetic fibers, plasticizers, resins, pharmaceuticals, etc. has made the demand for xylene increase tremendously over the past few decades. Unfortunately, current sources of xylene, which mainly comprise catalytic naphtha reforming and pyrolysis of gasoline, are unable to meet demand proportions for this important aromatic compound. *p*-Xylene in particular is a major chemical intermediate with rapidly growing demand, but it amounts to only 20–25% of a typical aromatics stream from naphtha reforming. As a result of this growing demand, alternative methods for enhancing the yield of xylene, especially the para isomer, are being investigated. Some of these alternatives include transalkylation of methyl benzenes with toluene, toluene disproportionation, and toluene methylation over zeolite based catalysts.[1] Though toluene disproportionation has produced significant xylene yield with remarkable *p*-xylene selectivity and has been applied industrially in processes like the MSTDP[2] and GT-STDP,[3] the formation of benzene as a coproduct is considered to be a major disadvantage. Toluene alkylation with methanol, on the other hand, produces a negligible amount of benzene and further makes use of a cheaper feed stock, methanol. Hence, toluene methylation is seen as an interesting alternative to both naphtha reforming and toluene disproportionation. However, in spite of the large volume of work done on toluene methylation regarding catalyst development,[4–8] reaction mechanism,[9–11] and kinetic studies,[12–17] the industrial application of the reaction is still not widespread, mainly because of the low levels of toluene conversion while maintaining high *p*-xylene selectivity. It has been estimated that a minimum of 25–30% toluene conversion while maintaining *p*-xylene selectivity of >85% is required for the process to be commercialized.[18]

Toluene methylation was initially investigated over various cationic forms of zeolite Y;[19,20] later; mainly medium-pore

zeolites of ZSM-5 structure with silicon isomorphously substituted by trivalent cations like Al, Fe, and B were used.[21] The interest in ZSM-5 is due to its superior shape-selectivity properties. Despite the large number of papers discussing the mechanism of toluene methylation, full details of the reaction mechanism are not yet known.[22] It is currently accepted that toluene ring alkylation with methanol over zeolites proceeds via chemisorption of methanol on the acid sites, followed by formation of surface-active species such as methoxy groups or methoxonium ions, which can further react with weakly adsorbed toluene.[23] Regarding the high *p*-xylene observed when ZSM-5 is used, generally, two basic models have been proposed to explain this observation. The first, as explained by Yashima et al.,[24] has to do with restrictions on the transition state to form *m*- and *o*-xylene inside the inner zeolite volume. The second explanation is related to diffusional differences between the xylene isomers.[25] It has been suggested that the high *p*-xylene diffusivity from the pores of zeolites increases the concentration of *o*- and *m*-xylene and, therefore, promotes their isomerization to *p*-xylene inside the pores of the catalyst. Mirth and Lircher[26] have reported that, for the shape-selective alkylation of toluene to *p*-xylene, the rate of the isomerization of *o*-and *m*-xylene in the pores of the zeolite must exceed the rate of alkylation.

In addition to catalyst development and the study of reaction mechanism, the kinetics of toluene methylation has also been studied over different zeolite types. One of the earliest kinetic models proposed for this reaction was that due to Wei.[12] With his model, Wei was able to predict *p*-xylene selectivity as a function of toluene conversion. Although Wei's model fitted well to experimental data from Young et al.[27] and Kaeding et al.,[28] it does not account for the reactions taking place on the external surface of the catalyst. Following this pioneering work, other kinetic models have been developed. Hashimoto et al.[13] developed a diffusion–kinetic model of the reaction, taking into consideration reactions both in the pores and on the external active centers. The model showed a good correlation with experimental data. Bhat et al.[14] carried out kinetic studies of toluene methylation over ZSM-8 catalyst in which they devel-

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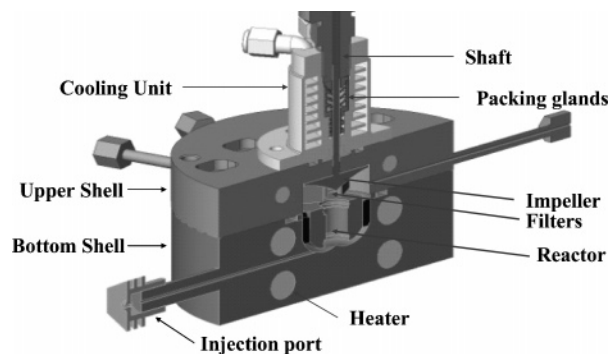
Figure 1. Schematic diagram of the riser simulator.

Table 1. Catalyst Characterization

catalyst	surface area (m^2/g)	Na$_2$O %	acidity (mmol/g)	% of weak acid site	% of strong acid site
fresh	70	negligible	0.23	62.5	37.5
precoked	63	negligible	0.18	66.67	33.33

oped a kinetic model for the reaction based on the Langmuir–Hinshelwood–Hougen–Watson approach with dual-site mechanism. They determined the activation energy of toluene methylation to be ~60.52 kJ/mol. Similarly, Ramakrishna et al.[15] developed a kinetic model for the reaction based on the Langmuir–Hinshelwood mechanism and found that the activation energy was ~79.83 kJ/mol over unmodified ZSM-5 catalyst. Furthermore, kinetic models for toluene methylation over modified ZSM-5 catalysts have also been studied. A good example is the work of Stelo and co-workers.[16] These workers developed a kinetic model for the reaction over Mg modified ZSM-5 catalyst based on a power law as well as the Redial-like mechanism and reported an activation energy of ~60.4 kJ/mol for the methylation reaction. In addition, they reported that the ratio of the rate constant of alkylation to that of the isomerization of p-xylene on the external surface of the catalyst was always >10. Young et al.[27] had proposed that, for para-selective catalysts, this ratio must be >3.

In most of the kinetic studies mentioned above, p-xylene is usually considered to be the only product of the alkylation reaction, while the other isomers are neglected. Moreover, virtually all of these studies were carried out in fixed-bed reactors where temperature and concentration gradients may have significant effects on the values of estimated model parameters, as pointed out by Ma and Savage.[29] Bearing all these in mind, we have decided to carry out a study of toluene methylation over fresh and precoked ZSM-5 based catalyst in a riser simulator in which temperature and concentration gradients are almost eliminated because of intense mixing. A comprehensive kinetic modeling of the reaction, which will account for all the important reaction steps including the formation of both m-and o-xylene, will also be carried out.

2. Experimental Section

2.1. Riser Simulator. All the experimental runs were carried out in the riser simulator of volume 45 cm^3(see Figure 1). This reactor is novel bench-scale equipment with an internal recycle unit invented by de Lasa.[30] A detailed description of the various riser simulator components, sequence of injection, and sampling can be found in the work by Kraemer.[31] The riser simulator operates in conjunction with a series of sampling valves that allow, following a predetermined sequence, one to inject reactants and withdraw products in short periods of time. The products were analyzed in an Agilent 6890N gas chromatograph
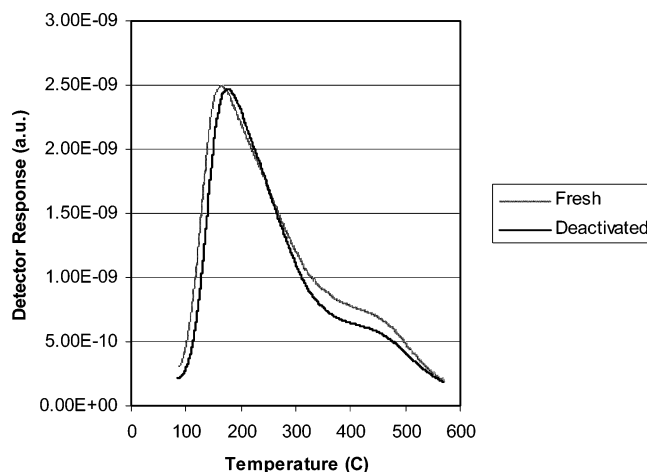

Figure 2. Comparison between the acidities of fresh and precoked catalyst.

with a flame ionization detector (FID) and a capillary column INNOWAX, 60 m cross-linked methyl silicone with an internal diameter of 0.32 mm.

2.2. Materials. 2.2.1. Catalyst Preparation/Characterization. The ZSM-5 zeolite used in this work was obtained commercially. The as-synthesized Na zeolite was ion-exchanged with NH$_4$NO$_3$ to replace the Na cation with NH$_4^+$. Following this, NH$_3$ was removed and the H form of the zeolite was spray-dried using kaolin and alumina as the filler and a silica sol as the binder. The resulting 60 μm catalyst particles had the following composition: 30 wt % zeolite, 50 wt % kaolin and alumina, and 20 wt % silica. The process of Na removal was repeated for the pelletized catalyst. Following this, the catalyst was calcined at 600 °C for 2 h. The total acidity was determined using NH$_3$ desorption method. The precoked catalyst was prepared by treating 80 mg of the fresh catalyst with 100 mL of carbonaceous 1,3,5-TIPB under mild reaction conditions (temperature 400 °C, reaction of 3 s.). 1,3,5-TIPB was used because its kinetic diameter is larger than the pore opening of ZSM-5, thereby restricting coke deposit to the external surface of the catalyst only. Hence, the internal active sites were not affected significantly by precoking. The amount of coke deposited on the catalyst from 1,3,5-TIPB was found to be 0.15 wt %. The total acidities and their distribution along with the measured Brunauer–Emmett–Teller (BET) surface areas for both the fresh and the precoked catalyst are summarized in Table 1, while Figure 2 shows a comparison between the acidities of fresh and precoked catalyst.

2.2.2. Feedstock. Analytical-grade (99% purity) pure toluene and methanol were obtained from Sigma-Aldrich. All chemicals were used as received, and no attempt was made to further purify the samples.

2.3. Procedure. 2.3.1. Fresh Catalyst. Catalytic experiments were carried out in the riser simulator with a feed of toluene/methanol molar ratio of 1:1 for residence times of 3, 5, 7, 10, 13, and 15 s at temperatures of 375, 425, 400, and 450 °C. Regarding the experimental procedure in the riser simulator, an 80 mg portion of the catalyst was weighed and loaded into the riser simulator basket (see Figure 1). The system was then sealed and tested for any pressure leaks by monitoring the pressure changes in the system. Furthermore, the reactor was heated to the desired reaction temperature. The vacuum box was also heated to ~250 °C and evacuated to a pressure of ~0.5 psi to prevent any condensation of hydrocarbons inside the box. The heating of the riser simulator was conducted under continuous flow of inert gas (Ar), and it usually takes a few hours until thermal equilibrium is finally attained. Meanwhile,
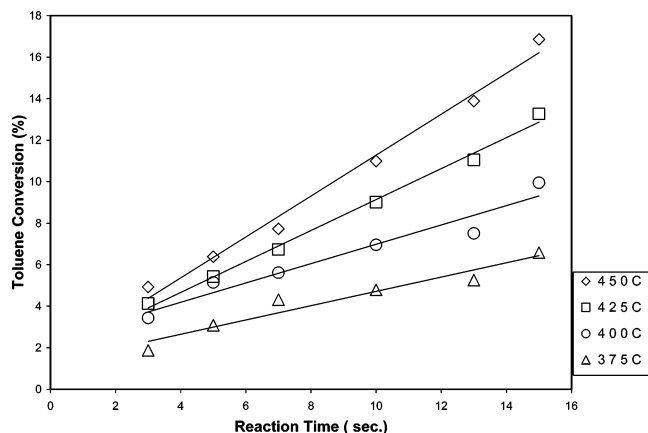
Figure 3. Effect of reaction conditions on toluene conversion.

Figure 4. Comparison of toluene conversions for fresh and precoked catalyst.

before the initial experimental run, the catalyst was activated for 15 min at 620 °C in a stream of Ar. The temperature controller was set to the desired reaction temperature, and in the same manner, the timer was adjusted to the desired reaction time. At this point, the GC is started and set to the desired conditions.

Once the reactor and the gas chromatograph have reached the desired operating conditions, 0.162 g of the feedstock was injected directly into the reactor via a loaded syringe. After the reaction, the four-port valve opens immediately, ensuring that the reaction was terminated and the entire product stream was sent online to the analytical equipment via a preheated vacuum box chamber.

2.3.2. Precoked Catalyst. Regarding experimental runs with the precoked catalyst, 100 mL of 1,3,5-TIPB was injected at 400 °C into the reactor after loading the reactor basket with 80 mg of fresh catalyst, and a limited reaction was allowed to take place for only 3 s. The system was then purged and cleaned with argon for 30 min. At this point, the reactor was heated to the desired reaction temperature. Once the reactor and the gas chromatograph have reached the desired operating conditions, the feedstock was injected directly into the reactor and a normal run was allowed to take place.

The amount of coke deposited on the spent catalysts was determined by a common combustion method. In this method, a carbon analyzer multi EA 2000 (Analytikjena) is used. Oxygen is supplied to the unit directly. A small amount of the spent catalyst (0.35 g) is used for the analysis. The coke laid out on the sample during reaction experiments is burned completely, converting the carbonaceous deposit into carbon dioxide. The amount of coke formed is determined by measuring the number of moles of carbon dioxide released. During the course of the investigation, a number of runs were repeated to check for reproducibility in the experimental results, which were found to be excellent. Typical errors were in the range of ±2%.

3. Results and Discussion

3.1. Toluene Conversion. The main products of the alkylation reaction were the three xylene isomers (para, ortho, meta) and trimethylbenzenes. Negligible amounts of benzene, ethylbenzene, cumene, and gaseous hydrocarbons were also detected. It was observed that, in spite of the short reaction times (3−15 s), substantial toluene conversions were obtained. Figure 3 shows the variation of toluene conversion with reaction time and temperature for the fresh catalyst. It is evident from this figure that toluene conversion increased with both reaction time and temperature, reaching a maximum of ∼16.8% at 450 °C

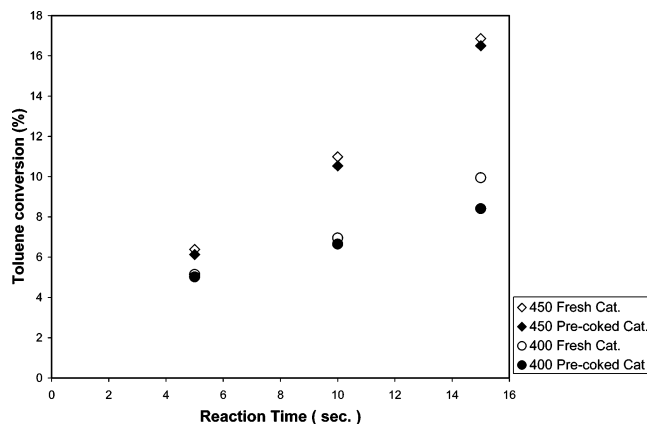for a reaction time of 15 s. For all the reaction temperatures, it was observed that conversion increased by ∼3−3.5 times when reaction time was increased from 3 to 15 s. Similarly, for all reaction times, toluene conversion was also found to increase as temperature was increased from 375 to 450 °C. Between 400 and 450 °C, it can be seen that the effect of temperature on the reaction became more significant with reaction time, as reflected by the divergence of the conversion curves as reaction time was increased from 3 to 15 s. Toluene conversions of approximately 16.8, 13.2, and 9.9% were achieved at 450, 425, and 400 °C, respectively, for a reaction time of 15 s.

Toluene conversion showed a similar dependence on temperature and reaction time over the precoked catalyst as with the fresh catalyst; however, the values were slightly lower than those over the fresh catalyst. Figure 4 compares toluene conversions over the fresh and precoked catalyst at temperatures of 400 and 450 °C for reaction times of 5, 10, and 15 s. From the figure, it can be seen that, at both 400 and 450 °C, precoking the catalyst had only a mild effect (<5% decrease) on toluene conversion, especially at reaction times less than 10 s. However, at 400 °C and a reaction time of 15 s, the difference in toluene conversion between the fresh and precoked catalyst became more visible, reaching up to 10%. The mild effect of catalyst precoking on toluene conversion is an indication that coke deposit was restricted to the external surface of the catalyst without interfering much with the acid sites within the pores of the catalyst where alkylation largely takes place. The slight decrease in toluene conversion can be attributed to the reduction of the total number of active sites due to partial deactivation and also due to problems of toluene diffusion, which may occur as a result of a possible blockage of some of the pore openings of the catalyst by the relatively larger molecules of 1,3,5-TIBP.

3.2. Xylene/TMB Yield. As shown in Figure 5, xylene yield, similarly to toluene conversion, increased with both reaction time and temperature over the fresh catalyst. A maximum xylene yield of ∼15.4% was achieved at 450 °C at 16.81% toluene conversion. This corresponds to a xylene selectivity of ∼92%. Furthermore, it was also noticed that, as temperature was increased from 375 to 450 °C, the ratio of xylene yield to that of trimethylbenzene decreased continuously, indicating that the secondary xylene alkylation with methanol to produce trimethylbenzene is highly sensitive to temperature. Figure 6 shows the variation of the ratio of xylene yield to the yield of trimethylbenzene with temperature for a reaction time of 15 s. From the figure, it can be seen that, as temperature was increased from 375 to 450 °C, the ratio dropped from ∼10.7 to ∼8.5.
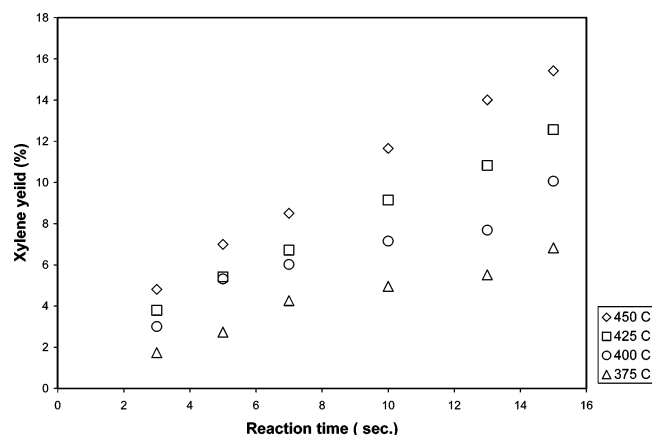
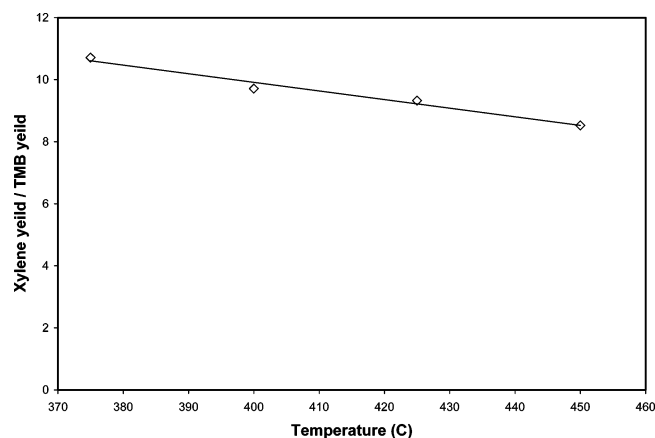**Figure 5.** Variation of xylene yield with reaction conditions.

Figure 6. Variation of xylene yield/TMB yield with temperature.

Figure 7. Effect of catalyst precoking on xylene/TMB ratio.
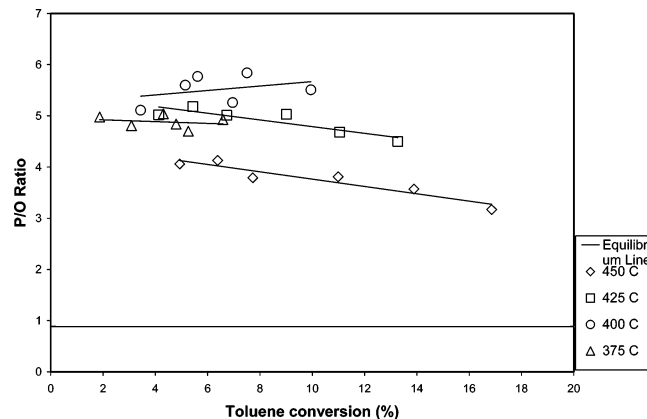
Figure 8. Variation of P/O with toluene conversion at different temperatures.

The fall of this ratio, which is a measure of xylene selectivity with temperature, has been widely reported by many researchers in the field. We had also noticed a similar drop in this ratio when we carried out toluene methylation over an USY-zeolite in the same riser simulator under identical conditions.

As can be seen from Table 2 parts a and b, it was found that precoking the catalyst increased the ratio of xylene yield/TMB yield as a result of the partial deactivation of the external surface of the catalyst, where xylene alkylation with methanol is believed to occur during toluene methylation. The formation of trimethylbenzene within the pores of ZSM-5 has been reported to be highly hindered, especially at low methanol concentration and short contact time.[15] Figure 7 compares the ratio of xylene yield/TMB yield for the fresh and precoked
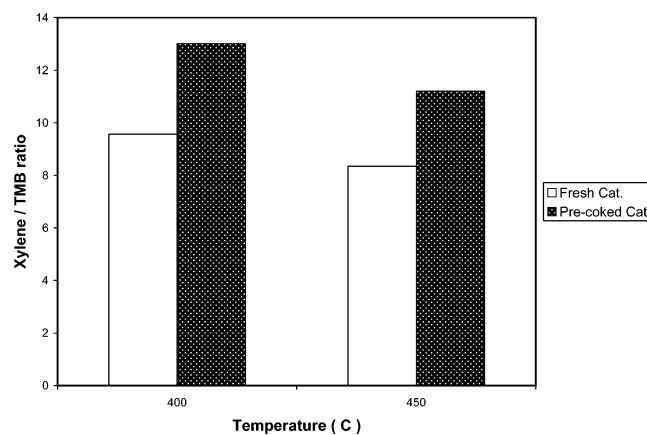
catalyst at 400 and 450 °C at a toluene conversion of 8%. From the figure, it can be seen that, at 400 °C, precoking the catalyst caused an increase in the ratio from ~9.6 to 13.0, representing a 36% increase. The effect of catalyst precoking on the ratio was less pronounced at 450 °C, with its value increasing from ~8.4 to 11.3, representing only a 25% increase.

3.3. *para*-Xylene/*ortho*-Xylene (P/O) Ratio. Figure 8 shows the variation of the P/O ratio with toluene conversion and reaction temperature. It is clear from this figure that, for all the reaction conditions investigated, P/O was found to be much higher than the equilibrium value, which was reported by Kaeding et al.[28] to be ~0.885 between 350 and 600 °C. A maximum P/O ratio of ~5.5 was achieved at 400 °C. The effect of temperature on the P/O ratio was very clearly visible. It was

Table 2. Product Distribution of Toluene Methylation over (a) the Fresh Catalyst and (b) the Precoked Catalyst at 450 and 400 °C, Toluene/ Methanol Ratio = 1:1, Approximate Weight Composition of Feed = (74.2% Toluene, 25.8% Methanol)

temp (°C)	time	yield (%)						toluene conversion (%)	P/O
		toluene	methanol	*p*-xylene	*o*-xylene	*m*-xylene	TMB		
				(a) Fresh Catalyst					
450	5	69.46	18.44	3.61	0.87	2.51	0.84	6.38	4.13
	10	66.05	15.13	5.77	1.52	4.37	1.41	10.99	3.81
	15	61.69	13.38	6.96	2.19	6.27	1.81	16.86	3.17
400	5	70.38	18.54	3.25	0.58	1.49	0.55	5.15	5.60
	10	69.04	16.29	4.33	0.82	2.00	0.75	6.96	5.26
	15	66.82	12.61	6.10	1.11	2.86	1.04	9.95	5.51
				(b) Precoked Catalysts					
450	5	69.53	19.64	3.90	0.84	2.53	0.64	6.29	4.66
	10	66.40	15.74	6.38	1.22	3.70	0.98	10.53	5.22
	15	61.73	13.11	7.63	1.90	5.44	1.36	16.81	4.02
400	5	70.48	20.01	2.71	0.38	0.91	0.31	5.02	7.23
	10	69.03	15.32	4.54	0.60	1.29	0.49	6.97	7.54
	15	67.96	13.25	5.45	0.75	1.65	0.59	8.41	7.28

found that, when temperature was initially increased from 375 to 400 °C, the P/O ratio measured at the same toluene conversion increased. However, when temperature was further raised beyond 400 °C, the ratio began to fall, reaching its minimum value at 450 °C. For example, at 6% toluene conversion, the values of P/O ratios at 375, 400, 425, and 450 °C were approximately 4.7, 5.5, 5.2, and 3.9, respectively. This observation can be explained in terms of the effect of temperature on the relative diffusivity of *p*- and *o*-xylene in the pores of ZSM-5. Although an equilibrium mixture of xylene is formed in the pores of the catalyst, the relative higher diffusivity of *p*-xylene as compared to that of *o*-xylene increases its composition in the primary product just outside the pores of the catalyst. Mirth et al.[32] had reported that diffusion plays an important role in the transport of the various xylene isomers in ZSM-5 at temperatures above 250 °C and that the diffusion coefficient of *p*-xylene can be up to 100 times that of *o*-xylene. Increasing temperature from 375 to 400 °C may cause an increase in the relative diffusivity difference between the two xylene isomers since the diffusivity of *p*-xylene is more sensitive to temperature than that of *o*-xylene. This can further enhance the P/O ratio. However, at temperatures beyond 400 °C, the diffusivity of *o*-xylene also becomes significant, thus reducing the diffusivity difference between the two xylene isomers with a net effect of a decrease in the P/O ratio. Recently, Al-Khattaf[33] proposed a similar explanation when he observed a drop in P/O ratio at temperatures beyond 400 °C during xylene transformation over ZSM-5 under reaction conditions similar to those of the present study. Another reason for the fall of the P/O at high temperatures may be due to the increased severity of the isomerization and disproportionation of *p*-xylene formed both within the pores and on the external surface of the catalyst.

As regards the variation of P/O ratio with toluene conversion, we observed that, at 400 °C and below, P/O was almost independent of toluene conversion. However, at 425 and 450 °C, the P/O ratio was found to decrease significantly as toluene conversion increased. From Figure 8, it can be seen that, at 450 °C, P/O decreased from ~4.0 at a toluene conversion of ~4.9% to ~3.1% at a toluene conversion of 16.8%. The observed fall in the P/O ratio with toluene conversion at temperatures above 400 °C may be due to the increased severity of the transformation of *p*-xylene formed, as explained above.

Furthermore, as expected, catalyst precoking was found to have a significant positive effect on the P/O ratio because of the partial deactivation of the external active sites, which are responsible for the undesirable isomerization of *p*-xylene selectively formed in the pores of the catalyst into the other isomers. Figure 9 compares the P/O ratio for the fresh and precoked catalyst at 400 and 450 °C for a toluene conversion of 8%. From the figure, it can be seen that, at 400 °C, the P/O ratio increased from ~5.5 to ~7.6, representing an increase of 27%. Similarly, at 450 °C, the effect of catalyst precoking was also clear, with P/O increasing from ~3.8 to 4.7, representing a 24% increase.

4. Kinetic Modeling

4.1. Model Development. In this section, a comprehensive kinetic model for toluene alkylation over the fresh ZSM-5 catalyst was developed. In developing the kinetic model, only the most important reactions taking place within the pores and on the external surface of the catalyst were considered. Toluene disproportionation was not considered, owing to the very low concentration of benzene in our reaction product. Furthermore,
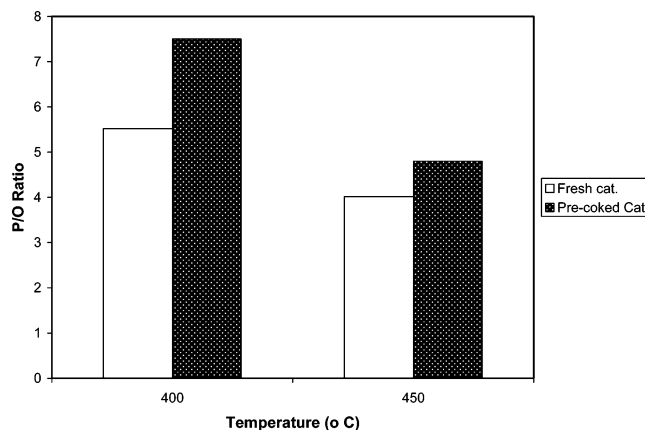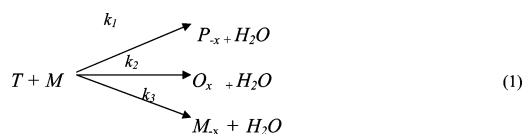

Figure 9. Effect of catalyst precoking on P/O ratio.

side transformations of methanol, like dehydration, have not also been considered, since these reactions hardly change the isomeric xylene distribution in our product.

4.2. Reactions inside the Pores of the Catalyst. 4.2.a. Toluene Alkylation. In most of the kinetic models developed for this reaction over ZSM-5, it is assumed that *p*-xylene is the only reaction product of toluene methylation and that *o*- and *m*-xylene are formed as a result of isomerization of *p*-xylene on the external surface of the catalyst.[14-16] However, it has been found that the isomerization of xylene and the production of *m*- and *o*-xylene are not entirely restricted to the crystal surface, because in addition to *p*-xylene, both *m*- and *o*-xylene are also sorbed in the volume of ZSM-5.[34] Mirth and Lercher[26] have observed by IR-spectroscopy that the concentrations of *m*- and *o*-xylene exceed that of *p*-xylene in the volume of ZSM-5. Therefore, we have included all three isomers in the alkylation step, as shown in eq 1.

$$
T + M
\begin{cases}
\xrightarrow{k_1} P_{-x} + H_2O \\
\xrightarrow{k_2} O_x + H_2O \\
\xrightarrow{k_3} M_{-x} + H_2O
\end{cases}
\quad (1)
$$

4.2.b. Internal Isomerization. Because of the relatively low diffusion rates of *m*- and *o*-xylene, they are almost completely isomerized to *p*-xylene before leaving the pores of the catalyst. We have represented these internal isomerizations of *o*- and *m*-xylene by eqs 2 and 3

$$
M_X \xrightarrow{k_4} P_X \quad (2)
$$

$$
O_X \xrightarrow{k_5} P_X \quad (3)
$$

4.3. Reactions on the External Surface of Catalyst. 4.3.a. Isomerization on the Catalyst Surface. The undesirable isomerization of *p*-xylene into the *m*- and *o*-isomers occurs on the catalyst crystal surface, where the shape-selectivity property is absent. These reactions are represented by eq 4 below:

$$
P_X
\begin{cases}
\xrightarrow{k_6} M_X \\
\xrightarrow{k_7} O_X
\end{cases}
\quad (4)
$$

4.3.b. Xylene Alkylation to Give TMB. As explained above, the formation of trimethylbenzene (TMB) in the pores of ZSM-5 is highly hindered. Therefore, its formation is limited to the external surface of the catalyst as a result of the reaction of

xylene with methanol. We assume that all the xylene isomers are converted to TMB at the same rate. Therefore, we have represented this reaction with a single equation, as shown below.

$$(M_X + O_X + P_X) + M \xrightarrow{k_8} TMB + H_2O \quad (5)$$
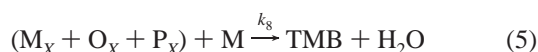
4.4. Rate Equations. On the basis of the equations above, the following catalytic rate equations can be written:

Rate of toluene disappearance, r_T

$$-r_T = -\eta \frac{V}{W_c} \frac{dc_T}{dt} = -\eta(k_1 c_T c_M + k_2 c_T c_M + k_3 c_T c_M)\varphi \quad (6)$$

Rate of p-xylene formation, r_{PX}

$$r_{PX} = \frac{V}{W_c} \frac{dc_{PX}}{dt} =$$
$$(\eta k_1 c_T c_M + k_4 c_{MX} + k_5 c_{OX} - (k_6 + k_7 + k_8)c_{PX})\varphi \quad (7)$$

Rate of o-xylene formation, r_{OX}

$$r_{OX} = \frac{V}{W_c} \frac{dc_{OX}}{dt} = (\eta k_2 c_T c_M - (k_5 + k_8)c_{OX} + k_7 c_{PX})\varphi \quad (8)$$

Rate of m-xylene formation, r_{MX}

$$r_{MX} = \frac{V}{W_c} \frac{dc_{MX}}{dt} = (\eta k_3 c_T c_M - (k_4 + k_8)c_{MX} + k_6 c_{PX})\varphi \quad (9)$$

Rate of trimethybenzene (TMB) formation, r_{TMB}

$$r_{TMB} = k_8(c_{PX}c_M + c_{OX}c_M + c_{MX}c_M)\varphi \quad (10)$$

where c_i = molar concentration of each of the species in the system, t = time, W_c = weight of catalyst, and φ = catalyst decay function, which accounts for the loss of catalytic activity as a result of deactivation due to coking. For the time-on-stream kinetic model employed in this work,

$$\varphi = \exp(-\alpha t) \quad (11)$$

where α = catalyst decay constant and V = volume of reactor. η = An effectiveness factor to account for the diffusion of toluene and methanol into the pores of the catalyst. Since m- and o-xylene are formed and isomerized within the pores of the catalyst, no effectiveness factor was defined for the reactions represented by eqs 2 and 3. Similarly, because the reactions represented by eqs 4 and 5 take place on the external surface of the catalyst, no effectiveness factor was also defined.

k_i are the temperature-dependent rate constants given by the Arrhenius relation below:

$$k_i = A_i \, e^{-E_i/RT} \quad (12)$$

The kinetic parameters obtained using eq 12 may show a mutual adverse effect of one parameter estimate (parameter correlation). Centering of some variables may often be helpful to reduce parameter interaction.[35] Agarwal and Brisk[36] showed that this reparametrization reduces the correlation between preexponential factors (A_i) and activation energies (E_i). Therefore, k_i constants were reparametrized by centering the temperature at an average reaction temperature of T_0,

$$k_i = k_0 \exp\left[\frac{-E_i}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (13)$$

where k_0 is the rate constant at T_0. Since the experimental runs were done at 375, 400, 425, and 450 °C, T_0 was calculated to be 412.5 °C.

By definition the molar concentration, c_i of every species in the system can be related to its mass fraction, y_i (measurable from GC), by the following relation

$$c_i = \frac{y_i W_{hc}}{V \cdot MW_i} \quad (14)$$

where W_{hc} = weight of feed stock injected into the reactor, MW_i = molecular weights of the individual species in the system, and V = volume of reactor.

Substituting eqs 11 and 14 into eqs 6−10 yields the following:

$$\frac{dy_T}{dt} [(-\eta k_1 y_T y_M + k_2 y_T y_M + k_3 y_T y_M)G_1] \exp(-\alpha t) \quad (15)$$

$$\frac{dy_{PX}}{dt} = [\eta G_2 k_1 y_T y_M + k_4 G_3 y_{MX} + k_5 G_3 y_{OX} - (k_6 + k_7 + k_8)y_{PX}G_3] \exp(-\alpha t) \quad (16)$$

$$\frac{dy_{OX}}{dt} = [(\eta G_2 k_2 y_T y_M - (k_5 + k_8)G_3 y_{OX} - k_7 G_3 y_{PX}] \exp(-\alpha t) \quad (17)$$

$$\frac{dy_{MX}}{dt} = [\eta G_2 k_3 y_T y_M - (k_4 + k_8)G_3 y_{MX} + k_6 y_{PX}G_3] \exp(-\alpha t) \quad (18)$$

$$\frac{dy_{TMB}}{dt} = k_8 G_4(y_{PX}y_M + y_{OX}y_M + y_{MX}y_M) \quad (19)$$

G_1, G_2, and G_3 are lumped constants given below:

$$G_1 = \left(\frac{W_{hc}W_c}{MW_M V^2}\right)$$

$$G_2 = \left(\frac{W_{hc}W_c MW_X}{MW_T MW_M V^2}\right)$$

$$G_3 = \frac{W_c}{V}$$

$$G_4 = \frac{W_{hc}W_c MW_{TMB}}{MW_X MW_M V^2}$$

Equations 15−19 contain 17 parameters, $A_1 - A_8$, $E_1 - E_8$, and α, which are to be determined by fitting into experimental data.

4.5. Assumptions. In developing this model, the following simplifying assumptions were made:

(1) Because of the short contact times, all the xylene isomerization steps were considered irreversible. This is justified since the concentrations of both m- and o-xylene (which are primarily produced by p-xylene isomerization on the surface of the catalyst) increased continuously with time. Al-Khattaf[37] recently used a similar approach in studying the kinetics of xylene isomerization in a riser simulator under conditions identical to those of the present study. The author modeled the

Table 3. Estimated Model Parameters

	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8
activation energy, E (kJ/mol)	56.83	67.11	79.42	31.50	32.00	25.16	25.24	24.49
95% CL	4.83	5.34	6.31	3.88	2.95	3.57	5.11	4.86
pre-exponential factor,^{a} $A_0 \times 10^4$ (m^3/(kg of catalyst)·s)	0.1435	0.0298	0.0880	0.3590	0.6975	0.0070	0.0086	8.8721
95% CL	0.0003	0.0001	0.0033	0.0044	0.0106	0.0034	0.0045	1.2990
catalyst deactivation constant (α)	0.0010							
95% CL	0.0005							

^{a} Pre-exponential factor as obtained from eq 13; unit for second order (m^6/(kg of catalyst)·s).

isomerization reactions based on reversible and irreversible reaction paths and found that the values of the estimated parameters were practically the same. A similar idea was used by Jose et al.[16] to account for *p*-xylene isomerization in their kinetic modeling of toluene methylation over Mg modified ZSM-5

(2) The effectiveness factor η was taken to be unity. This is justified by the fact that both toluene and methanol diffuse into the pores of ZSM-5 with negligible diffusion resistance. Jose et al.[16] have shown that, for toluene diffusion into ZSM-5, $\eta > 0.95$

(3) Reaction rates are considered to be first order in terms of toluene and xylene. A similar assumption has been made by previous workers in the area.[14-16]

4.6. Determination of Model Parameters. The 17 model parameters above were obtained by fitting experimental results into the rate eqs 15−19 using nonlinear regression (MATLAB package). The values of the 17 parameters along with their corresponding 95% confidence limits (CLs) are shown in Table 3. From the table, it can be seen that the activation energies for the formation of the three xylene isomers, E_1 (*p*-xylene), E_2 (*o*-xylene), and E_3 (*m*-xylene), follow the order of magnitude $E_3 > E_2 > E_1$. This is a reflection of the steric constraints on the formation of these xylene isomers due to the pore size of ZSM-5. *m*-Xylene, with the largest kinetic diameter, has the highest activation energy of 79.42 kJ/mol, followed by *o*-xylene with an activation energy of 67.11 kJ/mol; *p*-xylene, which has the smallest kinetic diameter, has the lowest activation energy of 56.83 kJ/mol. The difference in the estimated activation energies for the formation of *p*-xylene and *m*-xylene (∼22.59 kJ/mol) is in agreement with cluster DFT calculations carried out by Vos et al.,[22] which predicted that the activation energy of the formation of *p*-xylene is ∼20 kJ/mol lower than that of the other isomers. On the basis of the three activation energies, the average activation energy for toluene methylation was calculated to be 67.79 kJ/mol. This value is lower than the 79.83 kJ/mol reported by Ramakrishna et al.[15] over ZSM-5 but greater than the 60.52 kJ/mol reported by Bhat et al.[14] over ZSM-8. The majority of the kinetic studies of toluene methylation have reported activation energies of between 50 and 90 kJ/mol.[38]

The activation energies for the xylene isomerization steps represented by eqs 2−4 are generally much lower (25−32.00 kJ/mol) than those of the alkylation steps. As explained by Bhat et al.,[14] this can be due to the reaction mechanism. While toluene methylation follows a bimolecular mechanism that may require the adsorption of both toluene and methanol on adjacent sides of the catalyst active sites, xylene isomerization, on the other hand, can take place on the same sites where xylenes are formed. Furthermore, the values of our estimated activation energies for the isomerizations of *p*-xylene on the external surface of the catalyst (25.16 kJ/mol for *p*-xylene to *m*-xylene and 25.24 kJ/mol for *p*-xylene to *o*-xylene) are comparable to the values reported by Mantha et al.,[39] 28.3 kJ/mol, and Li et al.,[40] 21.4

kJ/mol for *p*-xylene to *o*-xylene and 17.9 kJ/mol for *p*-xylene to *m*-xylene over unmodified ZSM-5.

It is also important to point out the huge difference between the activation energies for toluene methylation (67.79 kJ/mol) and xylene methylation to form TMB (24.49 kJ/mol). Bhat also reported a similar huge difference. The difference in the activation energies for the two reactions may be an indication that the benzene ring of aromatic compounds becomes more reactive as the number of attached methyl groups increases so that xylene reacts more easily with methanol.

The *p*-xylene selectivity of toluene methylation as described by this model is highly dependent on the rate at which both *o*- and *m*-xylene formed in the pores of the catalyst are isomerized to *p*-xylene. It has been concluded by Mirth and other workers[10,26,41] that, for high *p*-xylene selectivity, the rates of these isomerization steps must exceed the rates of the alkylation steps that produce *o*- and *m*-xylene in the pores of the catalyst. We have observed that the ratio of the rate of *o*-xylene isomerization to *p*-xylene in the pores of the catalyst to the rate of its formation in the pores by alkylation (measured by k_5/k_2) was always >17 while the rate of isomerization of *m*-xylene to *p*-xylene in the pores of the catalyst to the rate of its formation (k_4/k_3) was always >3. Another important factor that determines the *p*-xylene selectivity is the ratio of the rate at which *p*-xylene is produced in the pores of the catalyst to the rate at which it is isomerized into the *m*- and *o*-isomers on the external surface of the catalyst. This ratio, which is measured by $k_1/(k_6 + k_7)$, was found to be always >6. For selective *p*-xylene toluene methylation, Young et al.[27] had proposed that this ratio must be >3.

The small value of α (0.001) obtained is an indication that catalyst deactivation due to coke deposit is negligible under our reaction conditions (small contact time). Measurement of coke deposit on the spent catalyst reveals that the maximum amount of coke deposit on the spent catalyst was 0.096%

To check the validity of the estimated kinetic parameters for use at conditions beyond those of the present study, the fitted parameters were substituted into the comprehensive model developed for this scheme and the equations were solved numerically using the fourth-order Runge−Kutta routine. The numerical results were compared with the experimental data and found to be in good agreement. Figure 10 shows a comparison between experimental data and our model predictions. Although it can be observed from this figure that the accuracy of the model decreases with temperature, it is, however, clear that, within the limits of experimental error, the model prediction compares very well with the experimental data, thus validating the correctness of the model. The decrease in the accuracy of the model with temperature can be attributed to the fact that secondary reactions like methanol dehydration, toluene disproportionation, and toluene dealkylation, which were not accounted for in developing the model, become more significant at temperatures of 450 °C and above than at lower temperature.
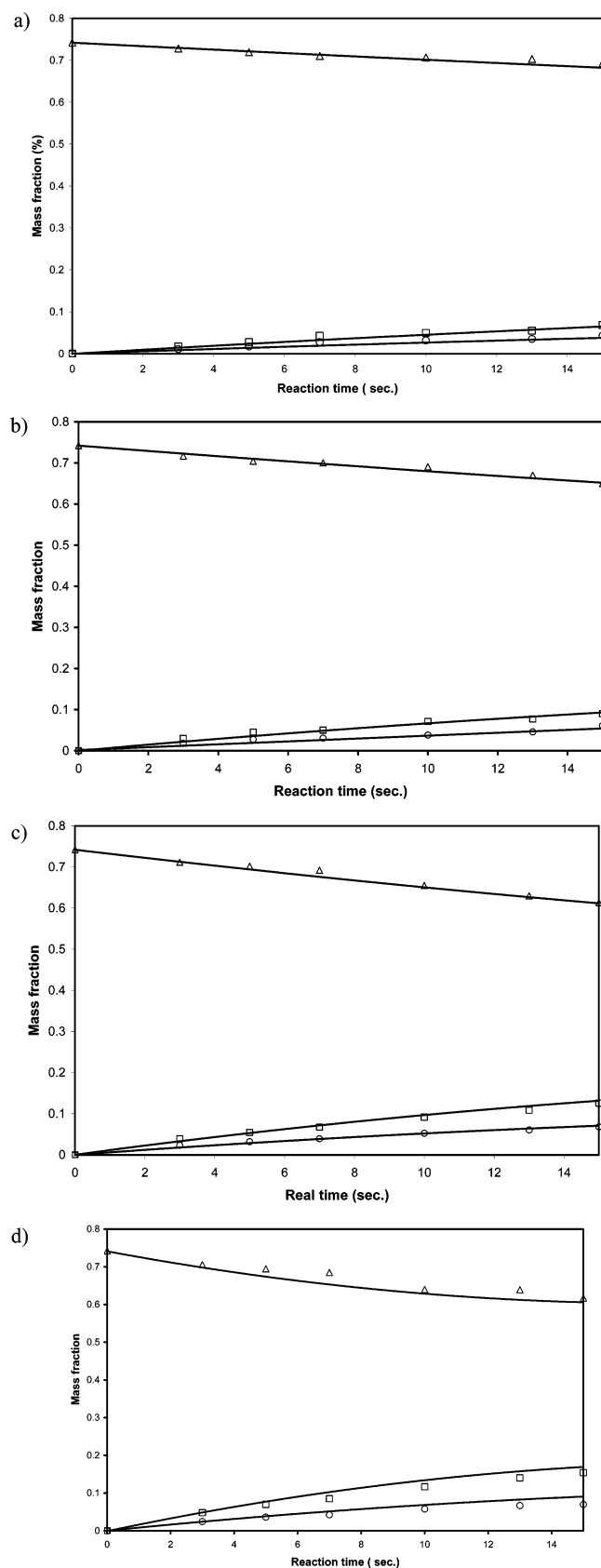
Figure 10. Comparison between experimental results and numerical simulations.

5. Conclusion

Toluene methylation has been studied over fresh and precoked ZSM-5 based catalyst in a riser simulator. The study was carried out over the temperature range of 375–450 °C. The following summarizes our major findings:

(1) Despite the short reaction times used (3–15 s), significant toluene conversion and xylene yield were achieved. Both toluene conversion and xylene yield were observed to increase with reaction temperature and time. Maximum toluene conversion and xylene yield of 16.81% and 15.41%, respectively, were obtained at 450 °C and reaction time of 15 s. This corresponds to xylene selectivity of ∼92%.

(2) The ratio of xylene/TMB in the reaction product was found to decrease as temperature was increased from 375 to 450 °C. This indicates that the alkylation of xylene with methanol to form TMB is highly sensitive to temperature

(3) The P/O ratio of the reaction product for a given reaction time was found to initially increase as temperature was increased from 375 to 400 °C and then to decrease as temperature was raised further beyond 400 °C. Furthermore, at reaction temperatures of 400 °C and below, P/O was found to be almost independent of toluene conversion. However, for reaction temperatures of 425 and 450 °C, P/O ratio decreased significantly as toluene conversion increased. A maximum P/O ratio of 5.5 was achieved at 400 °C for fresh catalyst.

(4) Partial deactivation of the active sites on the external of the catalyst crystal due to precoking was found to have a significant positive effect on both the xylene/TMB ratio and the P/O ratio. Measured at the same toluene conversion, P/O ratios for the precoked catalyst were found to be ∼25–30% higher than those of the fresh catalyst. Similarly, the xylene/TMB ratios for the precoked catalyst were found to be ∼25–36% higher than those of the fresh catalyst.

(5) The experimental results were modeled over the fresh catalyst based on a comprehensive reaction scheme using the time-on-stream model. The apparent activation energies for all the steps in the reaction scheme were determined. The average apparent activation energy for toluene methylation was found to be ∼67.79 kJ/mol

Nomenclature

C_i = concentration of species i in the riser simulator (mol/m^3)
CL = confidence limit
E_i = apparent activation energy of ith reaction, kJ/mol
k = apparent kinetic rate constant (m^3/kg$_{cat}$·s)
T = reaction temperature, K
T_o = average temperature of the experiment = 412.5 °C
k_0 = apparent kinetic rate constant (m^3/kg$_{cat}$·s) at T_o
A_i = pre-exponential factor (m^3/kg$_{cat}$·s), units based on first-order reaction
MW$_i$ = molecular weight of species i
R = universal gas constant, kJ/(kmol K)
t = reaction time (s)
V = volume of the riser (45 cm^3)
W_c = mass of the catalysts (0.81 g$_{cat}$)
W_{hc} = total mass of hydrocarbons injected in the riser (0.162 g)
y_i = mass fraction of ith component (wt %)

Chemical Species

TIBP =1,3,5-triisopropyl benzene

PX = *p*-xylene
OX = *o*-xylene
MX = *m*-xylene
TMB = trimethyl benzene
M = methanol
T = toluene

Ratios

P/O = ratio of *para*-xylene to *ortho*-xylene
P/M = ratio of *para*-xylene to *meta*-xylene

Greek Letters

α = apparent deactivation constant, s^{-1} (TOS model)

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