Kinetics of toluene methylation over USY-zeolite catalyst in a riser simulator

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Abstract

The kinetics of toluene alkylation has been studied in a riser simulator over a USY-zeolite-based catalyst. 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 both temperature and reaction time with maximum toluene conversion of 12.16% achieved at 450 °C for a reaction time of 15 s. Xylene selectivity, though almost independent of toluene conversion and reaction time was found to be significantly affected by temperature. It was found that xylene selectivity dropped from close to 100% to about 75% as temperature was increased from 375 to 450 °C. A non-equilibrium xylene distribution in the product with P/O and P/M ratios significantly higher than the equilibrium values were obtained. While P/O ratio increased as temperature was increased from 375 to 450 °C, P/M ratio on the other hand was found to decrease. Maximum P/O ratio of 1.63 and P/M ratio of 1.30 were obtained at 450 and 375 °C, respectively. The experimental results were modeled based on the time-on-stream catalyst decay function. The activation energy of toluene methylation was found to be 43.18 kJ/mol.
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1. Introduction

Xylene which comprises of three isomers; *para*, *ortho* and *meta* is considered one of the world's most important aromatic compounds. This is due to its increased application as a raw material for the production of a wide range of useful materials. *p*-Xylene, the most important of the three isomers is primarily used as a feedstock for terephthalic acid, a key component in polyethylene terephthalate (PET) resins. *o*-Xylene is used in plasticizers, medicines and dyes. *m*-Xylene is usually oxidized to isophthalic acid, which is used in unsaturated polyester resins (UPR).

The major sources of xylene are catalytic naphtha reforming and pyrolysis of gasoline [1]. However, xylene isomers from these sources generally do not match demand proportions as chemical intermediates, and further comprise of ethyl benzene, which is difficult to separate or convert [2]. *p*-Xylene in particular is a major chemical intermediate with rapidly growing demand, but amounts to only 20–25% of a typical aromatics stream from naphtha reforming. Ethyl benzene present in the xylene mixture is occasionally recovered for styrene production, but usually it is considered a less-desirable component of the aromatic stream [2]. The current objective of many aromatic complexes of increasing the yield of xylenes at the expense of compounds like benzene has led to the search for alternative sources to enhance the yield of xylene. Of particular interest are the toluene conversion processes comprising of toluene disproportionation and toluene alkylation with methanol over zeolite-based catalysts. Though toluene disproportionation has shown significant xylene yield, the formation of benzene as a co-product makes it less attractive when compared to toluene methylation. In addition to the formation of negligible amount of benzene, toluene methylation has the added advantage of using a cheaper and more abundant feedstock, methanol [3]. Therefore toluene methylation is seen as an alternative to both naphtha cracking and toluene disproportionation [4]. On this account, toluene methylation has been intensively studied as it is evident from the large number of publications on the topic.

The alkylation of toluene with methanol was initially studied by Yashima et al. [5] over cation exchanged zeolite Y; but later

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Nomenclature

C_i	concentration of specie 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)) = $\left(k_0' \exp\left[\frac{-E_R}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]\right)$
k_0'	Pre-exponential factor in Arrhenius equation defined at an average temperature [m^3/(kg cat s)], units based on first order reaction
MW$_i$	molecular weight of specie i
R	universal gas constant (kJ/(kmol K))
t	reaction time (s)
T	reaction temperature (K)
T_0	average temperature of the experiment
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 (0.166 g)
y_i	mass fraction of ith component (wt%)

Chemical species

W	water
M	methanol
T	toluene
TMB	trimethylbenzene
X	xylenes

Ratios

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

Greek letter

α	apparent deactivation constant (s^{-1}) (TOS Model)

mainly ZSM-5 was used because of its remarkable shape selectivity properties. It should be mentioned that the major objective of most toluene methylation processes is high toluene conversion while maintaining high yield of xylene, especially *p*-xylene. However, this has been difficult to achieve due to the existence of different side reactions such as, methanol dehydration and isomerization of primary reaction products which may contain high percentages of *p*-xylene if reaction is carried out over a shape selective zeolite such as ZSM-5. The latter side reaction usually leads to the formation of an equilibrium mixture of xylene containing approximately 23% *p*-xylene, 51% *m*-xylene and 26% *o*-xylene [6]. High *p*-xylene selectivity can be achieved through several catalyst modifications which include; incorporation of an oxide such as MgO, B$_2$O$_3$, or P$_2$O$_5$ [7], pre-coking by high-temperature, anaerobic treatment with a carbonaceous material [6], salanization [8] and steaming [9].

Much has been done in the area of catalyst development [6–9], reaction mechanism [10–12] and reaction kinetics [13–16]. A comprehensive review of the various aspects of toluene methylation has been carried out by Cejka and Wichterlova [17] and Llopis et al. [18]. However, in spite of all these studies, the commercial application of the toluene methylation is still not yet wide spread mainly because of the low conversion levels of toluene (maximum 8–10%) while achieving high *p*-xylene selectivity (>85%) [3]. This forbids the economic viability of the process, as the price difference between the raw material, toluene and the product, xylene is not very high. A minimum of about 25–30% toluene conversion is required to meet commercial requirements while maintaining *p*-xylene selectivity of more than 85% [3]. Efforts are on the way to make the process more commercially viable.

It is interesting to mention that until recently; virtually all works in the process development of toluene methylation have focused mainly on the use of fixed bed reactors. And in spite of the several potential advantages of using a fluidized bed, only a handful of research has been reported in this area. A fluidized bed process for toluene methylation can enhance reactant–catalyst contact which can result in higher rates of reaction and hence shorter reaction times. Also, extensive bed mixing and good heat distribution ensures uniform product quality. Moreover the use of short contact times can improve xylene selectivity by limiting side reactions like further xylene alkylation which can be detrimental to the yield of xylene. Another very important feature of the fluidized bed process is that it allows for easy and timely catalyst regeneration in contrast to the fixed bed process where catalyst regeneration is often laborious, expensive and time consuming [19]. This is particularly important given the fact that catalyst deactivation is one of the most serious challenges encountered in toluene methylation [20]. A few fluid bed processes of toluene alkylation with methanol have been reported to give improved toluene conversion and high xylene selectivity [21]. In view of these, we have decided to carry out a series of kinetic studies of toluene methylation over zeolite-based catalysts in a novel riser simulator which closely mimics the operation of commercial fluidized bed reactors. The present work studies the kinetics of toluene alkylation with methanol over a USY-based zeolite catalyst. The catalyst is a standard FCC catalyst. To the best of our knowledge, this is the first time this kind of work has been carried out.

2. Experimental procedure

2.1. The riser simulator

All the experimental runs were carried out in the riser simulator (see Fig. 1). The reactor is a novel bench-scale equipment with internal recycle unit invented by de Lasa [22]. The riser simulator consists of two outer shells, the lower section and the upper section which allow catalyst to be easily loaded or unloaded. The reactor was designed in such a way that an annular space is created between the outer portion of the basket and the inner part of the reactor shell. A metallic gasket seals the two chambers with an impeller located in the upper section. A packing gland assembly and a cooling jacket surrounding the shaft provide support for the impeller. Upon rotation of the shaft, gas
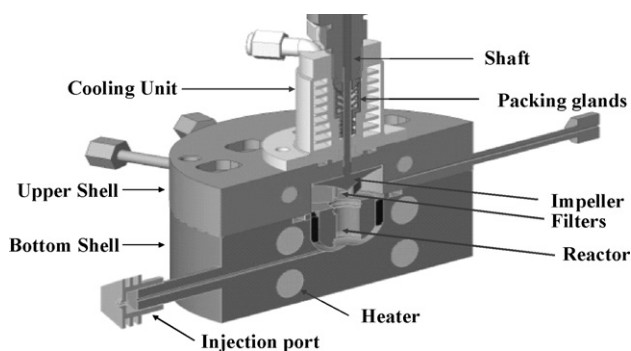
Fig. 1. Schematic diagram of the riser simulator.

is forced outward from the center of the impeller towards the walls. This creates a lower pressure in the center region of the impeller thus inducing a flow of gas upward through the catalyst chamber from the bottom of the reactor annular region where the pressure is slightly higher. The impeller provides a fluidized bed of catalyst particles as well as intense gas mixing inside the reactor. A detailed description of various riser simulator components, sequence of injection and sampling can be found in Kraemer [23].

2.2. Procedure

Regarding the experimental procedure in the riser simulator, 0.81 g of catalyst was weighed and loaded into the riser simulator basket. 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 around 250 °C and evacuated to around 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 gases (argon) and the process usually takes a few hours until thermal equilibrium is finally attained. Meanwhile, before the initial experimental run, the catalyst was activated for 15 min at 620 °C in a stream of air. 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, 200 μl (0.166 g) of the feedstock was injected directly into the reactor via a loaded syringe. After the reaction, a four-port valve connected to the reactor immediately opens ensuring that the reaction was terminated and the entire product stream sent on-line to the analytical equipment via a pre-heated vacuum box chamber. The products were analyzed in an Agilent 6890N gas chromatograph with a flame ionization detector and a capillary column INNOWAX, 60-m cross-linked methyl silicone with an internal diameter of 0.32 mm.

3. Results and discussion

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. 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%.

3.1. Catalyst preparation

Ultra stable Y zeolite (USY) was obtained from Tosoh Company. The Na-zeolite was ion exchanged with NH_4NO_3 to replace the sodium cation with NH_4^+. Following this, NH_3 was removed and the H form of the zeolite was spray-dried using kaolin as the filler and silica sol as the binder. The resulting 60-μm catalyst particles had the following composition: 30 wt% zeolite, 50 wt% kaolin and 20 wt% silica sol. The process of sodium removal was repeated for the palletized catalyst. Following this, the catalyst was calcined for 2 h at 600 °C. Finally, the fluidizable catalyst particles (60-μm average size) were treated with 100% steam at 760 °C for 5 h.

3.2. Catalyst characterization

Zeolite catalysts for use in fluidized-bed reactors are often incorporated in amorphous matrix to achieve the desired fluidization of the catalyst particles. As a result, the determination of the crystallinity and phase purity of the zeolite samples in the presence of this matrix is important in catalytic reactions. The BET surface area was measured according to the standard procedure ASTM D-3663, using Sorptomatic 1800 unit (Carlo Erba Strumentazione unit, Italy). The acid property of the catalyst was characterized by NH_3 temperature-programmed desorption (NH_3-TPD). In all the experiments, 50 mg of sample was out gassed at 400 °C for 30 min in flowing He and then cooled down to 150 °C. At that temperature, NH_3 was adsorbed on the sample by injecting pulses of 2 μl/pulse. The injection was repeated until the amount of NH_3 detected was the same for the last two injections. After the adsorption of NH_3 reached saturation, the sample was flushed at 150 °C for 1 h with He to remove excess NH_3, and then the temperature was programmed at 30 °C/min up to 1000 °C in flowing He at 30 ml/min. A Flame ionization detector was used to monitor the desorbed NH_3. The results of the catalyst characterization are summarized in Table 1.

3.3. Feedstock

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

3.4. Effect of reaction conditions on toluene conversion

Fig. 2 shows the variation of toluene conversion with reaction time and temperature. It is clearly evident that toluene conversion increased with reaction time for all the investigated temperatures. For example, at 400 °C, conversion increased from 1.42% to 8.05% (about 5.5 times) as reaction time was increased from 3 to 15 s. Also, from the figure, it can be observed

Table 1
Characterization of used catalyst

Catalyst	Acidity (mmol/g)	BET surface area (m^2/g)	Crystallite size (µm)	Unit cell size (Å)	SiO$_2$/Al$_2$O$_3$ (mol/mol)	Na$_2$O (wt%)
FCC-Y	0.033	155	0.9	24.27	5.7	Negligible
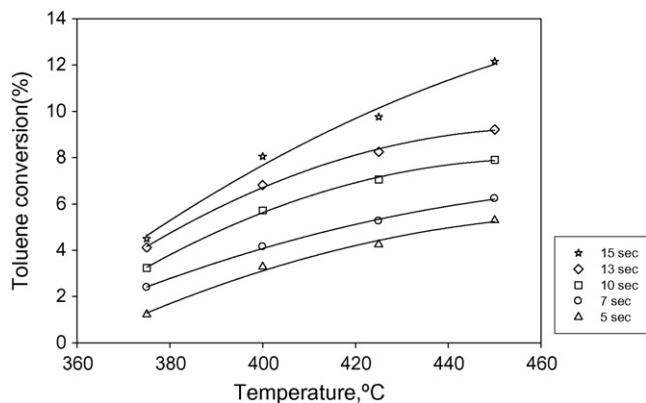
Fig. 2. Variation of toluene conversion with different reaction conditions.

Fig. 3. Variation of xylene selectivity with toluene conversion at different temperatures.

that for a given reaction time, toluene conversion increased with temperature. It could be noticed that conversion increased significantly as temperature was increased from 375 °C up to about 430 °C. However, beyond 430 °C, toluene conversion increased only slightly as temperature was increased. This may be attributed to the fact that at temperatures higher than 430 °C the rate of methanol decomposition becomes very high leaving insufficient methanol to alkylate the toluene. One other reason why toluene conversion increased only slightly when temperature rose beyond 430 °C is due to the fact that the secondary xylene dealkylation to form toluene becomes very significant at high temperatures thereby causing the equilibrium alkylation/dealkylation to shift towards dealkylation.

The maximum conversion achieved was 12.16% at 450 °C and reaction time of 15 s. This value is relatively high considering the low acidity (0.033 mmol/g) of the catalyst used. In general, toluene conversion is expected to increase with acidity. For example, Fechete et al. [24] carried toluene methylation over EMT-type zeolite and found that the less acidic zeolites showed lower activity (toluene conversion).

3.5. Xylene and TMB selectivity

Since the effectiveness of a toluene methylation process is measured in terms toluene conversion and the amount of xylene formed, xylene selectivity is defined based on toluene conversion according to Eq. (1)

$$\text{Xylene selectivity} = \frac{\text{weight of total xylene formed}}{\text{toluene conversion}} \times 100 \quad (1)$$

Similarly, trimethylbenzene (TMB) selectivity is defined as

$$\text{TMB selectivity} = \frac{\text{weight of total TMB formed}}{\text{toluene conversion}} \times 100 \quad (2)$$

Xylene selectivity was generally high (>75%) for all the reaction conditions investigated with selectivity approaching 100%
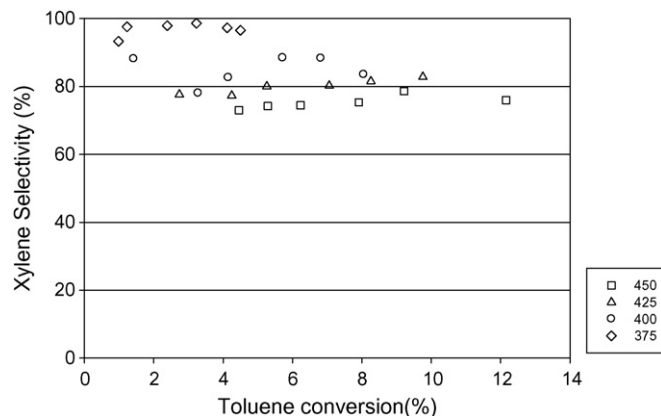
at 375 °C. While xylene selectivity was observed to decrease significantly with temperature, it remains largely insensitive to both reaction time and toluene conversion for a given temperature (Fig. 3). The selectivity of TMB on the other hand was generally low ranging from approximately 22% at 375 °C to a maximum of about 36% at 450 °C. Fig. 4 is a representative plot of xylene and TMB selectivity versus temperature for a reaction time of 15 s. It can be observed that xylene selectivity dropped from about 96% at 375 °C to approximately 75% at 450 °C. The fall in xylene selectivity with temperature can be attributed to the fact that competing secondary reactions like methanol dehydration, toluene disproportionation and xylene alkylation with methanol to form trimethylbenzene became more severe at high temperatures. As shown in Fig. 4, the fall in xylene selectivity with temperature is reflected in an increase in the selectivity of trimethylbenzene. From the figure, it can be seen that trimethylbenzene selectivity increased from 22% at 375 °C to approximately 36% at 450 °C.

Fig. 4. Variation of xylene and TMB selectivity with temperature for reaction time of 15 s.

3.6. Distribution of xylene isomers in reaction product

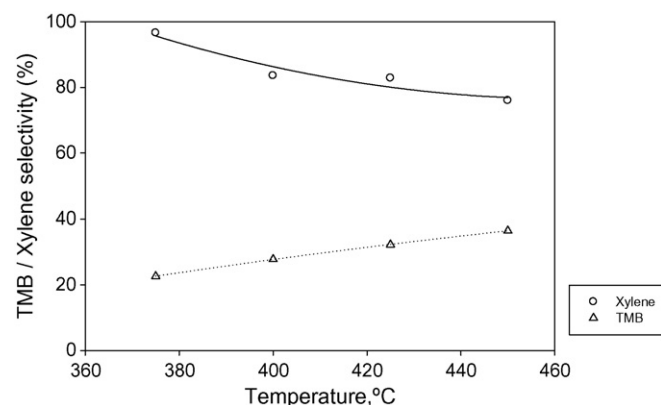Generally, it has been observed that when methanol and toluene are passed through a heated bed of unmodified zeolite-based catalyst (e.g. in a fixed bed reactor) an equilibrium mixture of xylene isomers are formed. Kaeding et al. [6] reported that over ZSM-5-based catalyst the equilibrium composition is approximately 23% *p*-xylene, 51% *m*-xylene and 26% *o*-xylene. This translates to P/O and P/M ratios of approximately 0.89 and 0.45, respectively. Usually, the low values of the P/O and P/M ratios are generally explained to be a result of further isomerization of *p*-xylene selectively produced in the pores of ZSM-5. It is therefore interesting that we have circumvented the equilibrium limitations posed on P/O and P/M ratios over a less shape selective Y-based zeolite with P/O and P/M ratios as high as 1.63 and 1.3, respectively, observed. The relatively high values of these ratios obtained in this work can be directly attributed to the short reaction times which limit further *p*-xylene isomerization into the other isomers. Furthermore, the composition of xylene isomers in the riser simulator depends on the nature of the reaction which produces the xylene. For example, Al-Khattaf et al. [25] recently studied the transformation of toluene and TMB to produce xylene in a riser simulator over a similar Y-based zeolite catalyst under reaction conditions identical to the ones used in this work and found that P/O ratio was always less than 1. Also, their earlier work [26] on *m*-xylene transformation in a riser simulator over Y-zeolite produced isomeric mixtures of xylene with a maximum P/O ratio of 1.

It should be noted that although xylene formed in the pores of the zeolite has equilibrium composition, the relative high rate of *p*-xylene diffusivity in the pores compared to that of the other isomers increases its composition in the primary product (just outside the pores of the zeolite). Several works have shown that the diffusivity of *p*-xylene in zeolites can be up to a 1000 times higher than that of the other isomers [27].

3.7. Effect of reaction conditions on P/O ratio

Fig. 5 shows the variation of P/O with toluene conversion at different temperatures. It can be observed that for all the
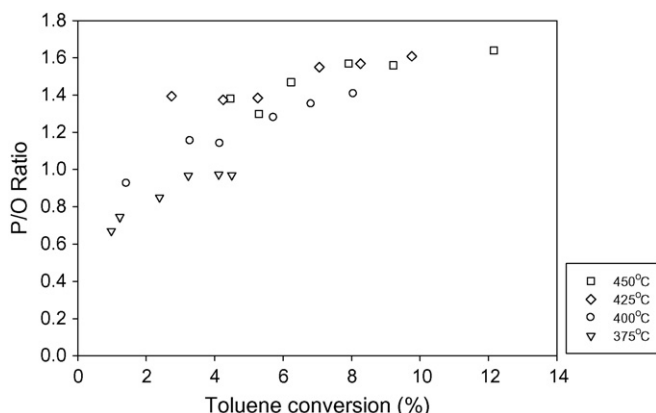

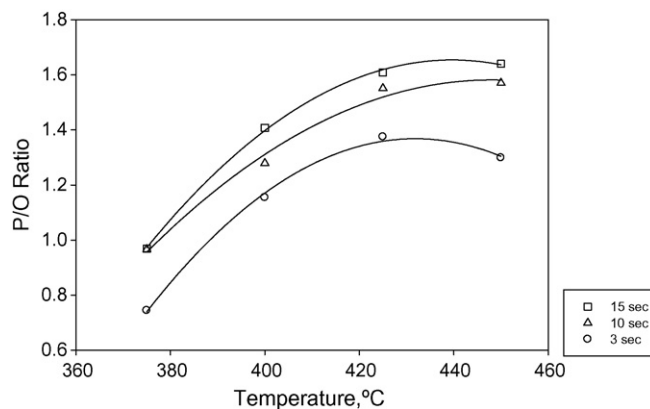Fig. 5. Variation of P/O with toluene conversion at different temperatures.

Fig. 6. Variation of P/O with temperature at different reaction times.

temperatures investigated, P/O increases slightly with toluene conversion and hence reaction time.

With regards to temperature, we observed that P/O ratios were lower than 1 at 375 °C, but increased with temperature well above the equilibrium value of 0.89 [6] approaching a maximum close to 450 °C. Fig. 6 shows the variation of P/O with temperature for reaction times of 15, 10 and 5 s. From the plot we observed that P/O increased sharply as temperature was initially increased from 375 °C to approximately 430 °C beyond which a further increase in temperature did not have much positive effect on the P/O ratio. This observation is explained in the following paragraph.

Theoretically, the alkylation of toluene with methanol is expected to give *p*- and *o*-xylene as primary products [14]. The selectivity in the primary alkylation step is governed by the reactivity of the individual positions for alkylation of the benzene ring and has been found to be *ortho/para* 2:1 [28]. In medium pore zeolites like ZSM-5, it is suggested that higher yields of *p*-xylene than *o*-xylene are obtained in the first alkylation step due to the restricted transition state selectivity [29]. However in a large pore zeolite like the one used in this work, the restriction on the formation of *o*-xylene is less pronounced allowing more *o*-xylene than *p*-xylene to be formed in the primary alkylation step. This is more pronounced at low temperatures with P/O ratios as low as 0.67 observed at 375 °C for reaction time of 3 s. As temperature was increased above 375 °C, the diffusivities of both *p*- and *o*-xylene increased. However, the rate at which the diffusivity of *p*-xylene increases is higher than that of *o*-xylene leading to a relative high diffusivity difference between the two isomers causing more *p*-xylene to be present in the primary product. This results in an increase of P/O ratio. At high temperatures beyond 430 °C, the diffusivity of *o*-xylene also becomes very significant thereby reducing the diffusion advantage of *p*-xylene over *o*-xylene. This dependence of diffusivity on temperature explains why increasing temperature above 430 °C did not have a significant positive effect on the P/O ratio.

3.7.1. Variation of P/M with reaction conditions

m-Xylene formed during methanol alkylation is essentially as a result of isomerization of the primary alkylation products namely; *p*- and *o*-xylene. Usually the primary products

Fig. 7. Variation of P/M with toluene conversion at different temperatures.

are isomerized until equilibrium is reached with P/M ratio of approximately 0.45 [6]. As stated above, we have been able to attain P/M ratio significantly higher than the equilibrium value.

Fig. 7 depicts the variation of toluene conversion with P/M ratio at different temperatures. As it can be seen from this figure, P/M remains almost insensitive to toluene conversion for a given temperature. The insensitivity of P/M (which is a measure of p-xylene selectivity) with toluene conversion is an interesting point to note since P/M is expected to fall over substantial toluene conversion due to further isomerization of p-xylene when it comes into contact with active sites on the external surface of the catalyst. In this work, we believe that p-xylene selectivity (as measured by P/M) remains insensitive to toluene conversion due to the high rate of gas fluidization in the riser simulator which significantly reduces the probability of p-xylene re-adsorption on the external active sites of the zeolite thereby restricting the chances of a further p-xylene isomerization.

Although P/M ratio was found to be insensitive to both toluene conversion and reaction time at a given temperature, variation of temperature was found to have a significant effect on this ratio. It was observed that for a given reaction time, the P/M ratio decreased as temperature was increased from 375 to 450 °C. For example, we observed that for a reaction time of 15 s, P/M ratio decreased from approximately 1.30 at 375 °C to about 0.99 at 450 °C. The decrease in P/M ratio with temperature can be attributed to increased severity of p-xylene isomerization with temperature.

4. Kinetic modeling

4.1. Model development

In addition to the main alkylation reaction (Eq. (3)), the side reactions (4)–(6) are also known to take place.

(a) Toluene alkylation with methanol

$$T + M \xrightarrow{k_1} X + W \tag{3}$$

(b) Xylene alkylation with methanol

$$X + M \xrightarrow{k_2} TMB + W \tag{4}$$

(c) Toluene disproportionation

$$T \xrightarrow{k_3} B + X \tag{5}$$

(d) Methanol dehydration

$$M \xrightarrow{k_4} G + W \tag{6}$$

Based on our product distribution and the fact that we have used short reaction times, the secondary reactions (5) and (6) were ignored and the following reaction scheme was proposed:

$$T + M \xrightarrow{k_1} X + W_{347}^{346}$$
$$+$$
$$M$$
$$\downarrow k_2$$
$$TMB + W$$

The experimental results were modeled based on the time-on-stream catalyst decay function. The following simplifying assumptions were made:

1. The reactor operates under isothermal conditions, justified by the negligible temperature change observed during the reactions.
2. A single deactivation function was defined for all the reactions taking place.
3. Contrary to the assumption that p-xylene is the only primary product of toluene methylation when ZSM-5 is used due to its microporosity [13,14], we assume that in this case, all the three isomers can be in the primary product. This is due to the large pore size of the zeolite used in this work which can accommodate the formation of all the isomers. Consequently all the xylene isomers were grouped into a single component, X.
4. A pseudo-first order of reaction was assumed for all the species.

Based on these assumptions, the following set of species balances and catalytic reactions can be written:

- Rate of toluene disappearance, r_T

$$-r_T = -\frac{V}{W_c}\frac{dc_T}{dt} = k_1 c_T c_M \varphi \tag{7}$$

- Rate of methanol disappearance, r_M

$$-r_M = -\frac{V}{W_c}\frac{dc_M}{dt} = (k_1 c_T c_M + k_2 c_X c_M)\varphi \tag{8}$$

- Rate of xylene formation, r_X

$$r_X = \frac{V}{W_c}\frac{dc_X}{dt} = (k_1 c_M c_T - k_2 c_X c_M)\varphi \tag{9}$$

- Rate of trimethylbenzene, TMB formation, r_{TMB}

$$r_{TMB} = \frac{V}{W_c}\frac{dc_{TMB}}{dt} = (k_2 c_X c_M)\varphi \tag{10}$$

where c_i is the molar concentration of each of the species in the system; t the time; W_c the weight of catalyst; and φ is the 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,

$$\varphi = \exp(-\alpha t) \tag{11}$$

where α is the catalyst decay constant which measures the severity of coking and k_i are temperature dependent rate constants given by the Arrhenius relation below:

$$k_i = k_{0,i}\, e^{-E_i/RT} \tag{12}$$

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 [30]. Agarwal and Brisk [31] showed that this reparameterization reduces the correlation between pre-exponential factors and activation energies. Therefore, k_i constants were re-parameterized by centering the temperature at an average reaction temperature of T_0.

$$k_i = k_{0i} \exp\left[\frac{-E_i}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{13}$$

By definition the molar concentration, c_i of every species in the system can be related to its mass fraction, y_i by the following relation:

$$c_i = \frac{y_i W_{hc}}{V\, MW_i} \tag{14}$$

where W_{hc} is the weight of feedstock injected into the reactor, MW_i the molecular weights of the individual specie in the system, and V is the volume of reactor.

Substituting Eqs. (11) and (14) into Eqs. (7)–(10), we have the following:

$$\frac{dy_T}{dt} = -k_1 y_M y_T G_1 \exp(-\alpha t) \tag{15}$$

$$\frac{dy_M}{dt} = -(k_1 y_M y_T G_2 + k_2 y_X y_M G_3)\exp(-\alpha t) \tag{16}$$

$$\frac{dy_X}{dt} = (k_1 y_M y_T G_4 + k_2 y_X y_M G_5)\exp(-\alpha t) \tag{17}$$

$$\frac{dy_{TMB}}{dt} = -k_2 y_X y_M G_6 \exp(-\alpha t) \tag{18}$$

In Eqs. (15)–(18), G_1 to G_6 are lumped constants given as follows:

$$G_1 = \frac{W_c W_{hc}}{MW_M\, V^2} \tag{19}$$

$$G_2 = \frac{W_c W_{hc}}{MW_T} \tag{20}$$

$$G_3 = \frac{W_c W_{hc}}{MW_X\, V^2} \tag{21}$$

$$G_4 = \frac{W_{hc} W_c\, MW_X}{MW_M\, MW_T\, V^2} \tag{22}$$

$$G_4 = \frac{W_{hc} W_c\, MW_X}{MW_X\, MW_M\, V^2} \tag{23}$$

The constants k_1 and k_2 are obtained from Eq. (13) as

$$k_1 = k_{01} \exp\left[\frac{-E_1}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

$$k_2 = k_{02} \exp\left[\frac{-E_2}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

Eqs. (15)–(18) contain five parameters; k_{01}: pre-exponential coefficient for toluene methylation; k_{02}: pre-exponential coefficient for TMB formation; E_1: activation energy of toluene methylation; E_2: activation energy for TMB formation; α: catalyst decay constant which is an indication of the severity of coking.

4.2. Determination of model parameters

The five model parameters above were obtained by fitting experimental results into the rate equations (15)–(18) using nonlinear regression (MATLAB package). The values of the five parameters along with their corresponding 95% confidence limits (CL) are shown in Table 2. From the table, it can be seen that the activation energy of toluene methylation; 43.18 kJ/mol is only slightly higher than that for xylene alkylation to TMB; 41.20 kJ/mol. Although it may not be appropriate to compare the values of the activation energies obtained in this work with those generally reported in literature owing to difference in our system and the kind of catalyst used, it is however worth noting that our values are not far from those reported in literature. For example Bhat et al. [14] have reported activation energy of 60.52 kJ/mol for toluene methylation over HZSM-8 while Mantha et al. [13] reported a value of 79.83 kJ/mol over HZSM-5. In both cases, p-xylene was considered to be the only primary product. It should be noted that the value which we have reported is the average

Table 2
Estimated kinetic parameters based on time-on-stream (TOS Model)

	Parameters				
	E_1 (kJ/mol)	E_2 (kJ/mol)	$k_{01} \times 10^3$ (m³/(kg cat s))[a]	$k_{02} \times 10^3$ (m³/(kg cat s))	α
Values	43.18	41.20	0.0186	0.1037	0.0166
95% CL $\times 10^3$	1.62	7.90	0.003	0.0304	0.0269

[a] Pre-exponential factor as obtained from Eq. (13); unit for second order (m⁶/(kg cat s)).
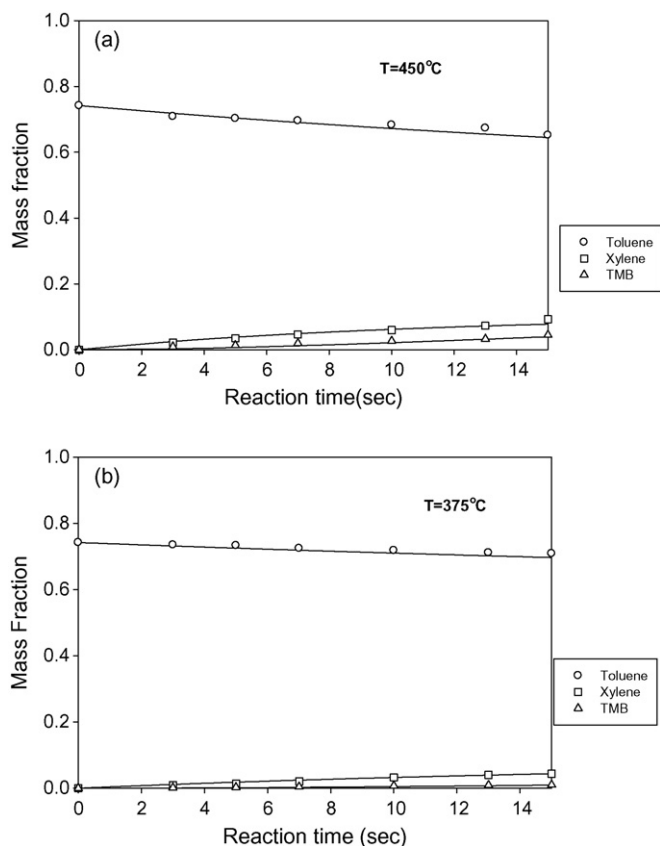
Fig. 8. Comparison between experimental data and model predictions (—). (a) $T = 450\,^\circ C$ and (b) $T = 375\,^\circ C$; (○) toluene; (□) xylene; (△) TMB.

apparent activation energy for the formation of all the three isomers. The low value of our apparent activation energy may be attributed to the reduced mass transfer resistance due to the relative larger pore size of the zeolite used as compared to ZSM-8 and ZSM-5 used in [13,14].

The small value (0.0166) of the catalyst decay constant, α is an indication of negligible catalyst coking. Generally, significant coking is expected to occur over a large pore zeolite like the one used in this work. This is because zeolites with large pores used in toluene methylation provide room for the formation of polynuclear aromatics which are important coke precursors [32]. The low level of coking may be attributed to the negligible amount of gaseous hydrocarbons (olefin) observed in our reaction product. Usually, the condensation of olefins and aromatics in the pores of zeolites are responsible for the formation of polynuclear aromatic coke precursors.

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 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. Fig. 8 shows a comparison between experimental data and our model prediction at 450 and 375 °C. It is clear from this figure that the model prediction compares very well with the experimental data thus validating our model.

5. Conclusion

The kinetics of toluene methylation has been studied in a riser simulator which closely mimics the operation of commercial fluid bed reactors. The study was carried out over an USY zeolite-based catalyst over the temperature range of 375–450 °C. We were able to show that even a non-optimized catalyst with low shape selectivity properties can perform exceptionally well in a fluidized bed process of toluene methylation. The following summarizes our major findings:

(1) In spite of the low acidity of catalyst used (0.033 mmol/g), significant toluene methylation reaction was observed with toluene conversion as high as 12.16% obtained at 450 °C for reaction time 15 s.
(2) It was observed that xylene selectivity was almost independent of both reaction time and toluene conversion but highly dependent on reaction temperature. High xylene selectivity close to 100% was obtained at 375 °C. However, selectivity fell to about 75% at 450 °C.
(3) Toluene methylation in the riser simulator produced a non-equilibrium xylene distribution in the product with P/O and P/M ratios significantly higher than the equilibrium values obtained. Maximum P/O ratio of 1.63 was obtained at 450 °C while maximum P/M ratio of 1.3 was obtained at 375 °C. Furthermore, it was observed that P/O ratio decreased as temperature decreased from 450 to 375 °C while P/M was found to increase.
(4) The experimental results were modeled based on the time-on-stream catalyst decay function. The activation energy of toluene methylation was found to be 43.18 kJ/mol.

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