

Enhancing *P*-xylene selectivity during *m*-xylene transformation using mildly pre-coked ZSM-5 catalyst

S. Al-Khattaf*

Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia.

Abstract

In the present work, the transformation of *m*-xylene was studied over fresh and pre-coked H-ZSM-5 catalyst in a riser simulator over the temperature range of 350-500°C. Significant differences were observed in both the activity and product selectivity pattern for the two forms of the catalyst. While, the fresh catalyst generally gave higher *m*-xylene conversion, the pre-coked catalyst produced higher Isomerization/Disproportionation (I/D) and Para/ Ortho xylene (P/O) ratios. For both forms of the catalyst, *m*-xylene conversion was found to increase with both reaction temperature and reaction time (0-15 s). A maximum conversion of 30.8% was achieved at 500°C for a reaction time of 15 s using the fresh catalyst. The corresponding value for the pre-coked catalyst was 24.6%. P/O and I/D ratios as high as 2.5 and 10 respectively were observed with the pre-coked catalyst. It was also observed that the P/O and I/D ratios decreased with increasing temperature for both catalyst and that the difference between these ratios for the two catalysts is more pronounced between 400 and 450°C than at higher temperatures. Kinetic modeling of the *m*-xylene transformation over the pre-coked catalyst yielded a lower activation energy for *p*-xylene formation compared to the fresh catalyst. And an activation energy of 17.5 kcal/mol for the of *m*-xylene disproportionation was obtained for the pre-coked catalyst compared to 7.82 kcal/mol for the fresh catalyst. These values are indicative of the restriction posed on disproportionation by the pre-coked catalyst as reflected by higher I/D ratios.

Keywords: *m*-Xylene transformation, ZSM-5 zeolite, isomerization, disproportionation, Pre-coking.

*Corresponding author. Tel.: +966-3-8601429; fax: +966-3- 8604234
E-mail address: skhattaf@kfupm.edu.sa

1. Introduction

With increasing demand for p-xylene as a starting materials for various processes, like the production of synthetic fibres and plasticizers, efforts are continually been directed to selectively produce p-xylene from low valued m- and o-xylenes. Unfortunately, the amount of p-xylene theoretically obtainable from these aromatic compounds is very much limited by thermodynamics. Consequently, attempts to overcome thermodynamic limitations in the transformation of xylenes have indeed constituted a great challenge to both the academic and petrochemical industry. However, the introduction of Mobil's selective toluene disproportionation process "MSTDP" in 1988 represented a clear technological improvement [1]. It should be mentioned that toluene alkylation with methanol over ZSM-5 was the first test reaction used by Chen [2] to demonstrate para-selectivity [1,2].

It is well-known that xylenes undergo two main competitive reactions over zeolite catalysts. Isomerization which produces p and o-xylens and disproportionation producing toluene and trimethylbenzenes. The shape selective conversion of xylenes over ZSM-5 has been investigated in detail by several workers [1-12]. Modifications of ZSM-5 by various compounds have been employed to enhance p-xylene selectivity from xylene transformation process [13-16]. Similarly, para selectivity has been improved by the selective coking of the external surface of ZSM-5 [17-22].

The use of ZSM-5 zeolite was reported to enhance the isomerization reactions at the expenses of disproportionation reaction and it was also noticed to be more selective to p-xylene than o-xylene [23]. Furthermore, the zeolite pretreatment or modification was found to further boost the zeolite shape selectivity [3-6,24]. For example, it is well known that p-xylene is 1000 to 10000 times faster in diffusion than both m and o xylems [11,24, 25]. In view of this the effectiveness factor was estimated to be around 1, 0.05 and 0.4 (at 450°C) for the reaction of p-xylene, m-xylene and o-xylene respectively [25]. Hindering diffusion in ZSM-5 pores by reducing the channel size and increasing

diffusional pathway can logically lead to increment in isomerization selectivity over the bulky disproportionation reaction and also in p-xylene selectivity over o-xylene selectivity. Hence the diffusivity control can be used in principle [24] to enhance p-xylene selectivity. Tsi et al [24] reported several ways to control this diffusivity. Among these methods are the use of large zeolite crystal size, pre-coking pretreatment and silica deposition on the ZSM-5 surface. Pre-coking, for example is claimed to increase p-xylene selectivity up to 70-80%. Haag et al. [20, 21] were able to increase p-xylene selectivity by 79% by pre-coking over ZSM-5 during toluene disproportionation.

Regarding pre-coking, it is believed that coke selectively deposits on the zeolite external surface covering the external active sites by introducing the suitable molecules. It has been reported that certain large molecules can not penetrate into the zeolite structure thus they react on the external available sites forming coke which covers those sites used for p-xylene transformation (undesired secondary reaction) [26,24]. Since coke deposits only externally, it is assumed that the internal sites stay essentially unchanged. Thus pre-coking, generally reduces the total acid site number but it keeps enough acid sites to catalyze the reaction [26,24]. Niwa et al [27] on the other hand, concluded that narrowing zeolite opening pores can affect p-xylene selectivity much more than inactivation of the external acid sites.

Pre-coking strategy was applied industrially in MSTDPSM process. It was reported that p-xylene selectivity reached 82% at 30 % toluene conversion during toluene disproportionation. Furthermore, it reached up to 90% at the end of the run period where the toluene conversion is about 25% [24]. It was reported that for toluene disproportionation reaction over HZSM-5, a coke content of around 2 wt% is needed for para- selectivity enhancement [21,28]. Bauer et al [7] argued that an additional thermal treatment of the pre-coked HZSM-5 by hydrogen or alkanes is effective in

enhancing p-xylene selectivity and only a small amount of coke is needed for the treatment (around 0.3 wt%).

In pre-coking, the catalyst is initially contacted with certain feedstock at certain reaction conditions to deposit a certain amount of coke on the catalyst. It has to be kept in mind that large amount of coke have the ability to deactivate even the internal active sites [12]. Thus pre-coking process has to be carefully controlled in order not to produce a negative effect. Surveying the present literature on the isomerization of xylenes over pre-coked catalyst, it appears that systematic studies which focus on the influence of the reaction parameters (reaction time, temperature, and conversion) are scarce. Thus, with this in mind, a systematic study on the influence of reaction parameters and pre-coking on the isomerization and disproportionation selectivity during the transformation of the m-xylene will be investigated. Modelling the pre-coked catalysed reaction will also be conducted. 1,3,5 tri-isopropyl-benzene (TIPB) will be used to deactivate the external active sites.

2. Experimental Section

2.1 The riser simulator

All the experimental runs were carried out in the riser simulator (see Fig. 1). This reactor is novel bench scale equipment with internal recycle unit invented by de Lasa [29]. A detailed description of various riser simulator components, sequence of injection and sampling can be found in the work by Kraemer [30]. 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 with a flame ionization detector and a capillary column INNOWAX, 60-m cross-linked methyl silicone with an internal diameter of 0.32 mm.

2.2 Materials

The ZSM-5 zeolite used in this work was provided by Grace Davison Co. The as-synthesized Na zeolite was ion exchanged with NH_4NO_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 amount of desorbed NH_3 (total acidity). *Fig 2 shows comparison between the acidity of fresh and pre-coked catalyst. Total acidity and its distribution along with the measured BET surface area for both the fresh and the pre-coked catalyst are summarized in Table 1.*

2.3. Procedure

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 Fig. 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 around 250°C and evacuated to a pressure of 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 gas (Ar), and it 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 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, the feedstock was injected directly into the reactor via a loaded syringe. After the reaction, the four-port

valve immediately opens, ensuring that the reaction was terminated and the entire product stream sent online to the analytical equipment via a preheated vacuum box chamber.

2.4. Pre-coking experiments

Regarding pre-coking runs, 100 ml of 1,3,5-TIPB was injected at 400°C and limited reaction was allowed to take place for only 3 sec. The amount of coke deposited on the catalyst from 1,3,5 TIPB was found to be 0.15 wt % . 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 (m-xylene) 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 moles of carbon dioxide.

3 Results and Discussion

3.1 m-xylene conversion

The major reaction products of the transformations of m-xylene, on fresh catalyst are: the other two xylene isomers (isomerization), trimethylbenzenes and toluene (disproportionation). The conversion obtained for m- xylene (without deactivation) is shown in Fig. 3 for different reaction time and temperature.

It is clear that m-xylene conversion increases with both reaction time and temperature. For example at 15sec, the m-xylene conversion was found to be around 20%, 25% and 30% at 400, 450 and 500C respectively. As temperature increases the conversion is also increased. The effect of reaction contact time was also very clear. For all reaction temperatures, the conversion is significantly

increased with contact time. For example, increasing contact time from 3 sec to 15 sec increased conversion about 3-4 times for all reaction temperatures investigated.

The effect of catalyst pre-coking via 1,3,5 TIPB on m-xylene conversion for contact times of 5, 10 and 15 sec is shown also in Fig 3 at 400°C and 500°C respectively. It can be seen that for a reaction time of 15s and a temperature of 500°C, the fresh catalyst gave 30% m-xylene conversion, while the pre-coked catalysts gave around 25 % conversion. As expected coke coming from the bulky 1,3,5-TIPB has virtually deactivated the external active sites. Furthermore, coking via 1,3,5 TIPB can cause complete blockage for the zeolite internal channels keeping in mind that 1,3,5 TIPB can not diffuse inside ZSM-5 pore structure.

3.2 Isomerization to disproportionation (I/D) ratio

The transformation of xylenes over zeolite catalysts proceeds via two major reactions namely: isomerization and disproportionation. Disproportionation reaction requires two molecules of xylene reactants in a bulky bimolecular transition state intermediate. As a result, disproportionation is significant only on large pore zeolites that can accommodate these intermediates. Furthermore, since disproportionation is a bimolecular reaction, an increase in the number of active sites would enhance this reaction. It has to be mentioned that several researchers suggested that D/I ratio on ZSM-5 approaches zero due to its small pores and channel intersection [34,35]. However, Bauer et al [7,12] observed TMBs on their nano ZSM-5. Also in the present study TMBs have been observed keeping in mind that the catalyst used is ZSM-5 dispersed in kaolin and acidic alumin (large pores) matrix. The effect of temperature and conversion on I/D ratio is shown in Fig. 4. It can be seen from this figure, that I/D decreases with reaction temperature while conversion has a mild effect on this ratio. The decrease of I/D with temperature indicates that disproportionation reaction is more sensitive to

temperature than isomerization. This observation is in line with the fact that disproportionation requires a higher energy of activation as compared to isomerization reaction [31-33].

Fig 4 also shows the effect of catalyst deactivation on I/D ratio. I/D ratio for both the fresh catalyst and the partially deactivated catalysts are not much affected by m-xylene conversion. Furthermore, I/D ratio for the partially deactivated catalyst changes drastically with temperature. For example, at 10% conversion, this ratio decreases from 7.5 to 1.8 by increasing the temperature from 400 to 500°C.

Furthermore Fig 4 shows that I/D ratios for the deactivated catalysts are much higher than that of the fresh catalyst. The decrease in disproportionation can be easily explained based on the fact that this reaction requires two adjacent active sites to take place. Partial coking covers some of these sites leading to a decrease in disproportionation rate. Guisnet and co-workers [36] reported opposite conclusion when HFAU zeolites were used for m-xylene transformation. Their result was attributed to the greater selectivity of strong acid sites to monomolecular isomerization reaction.

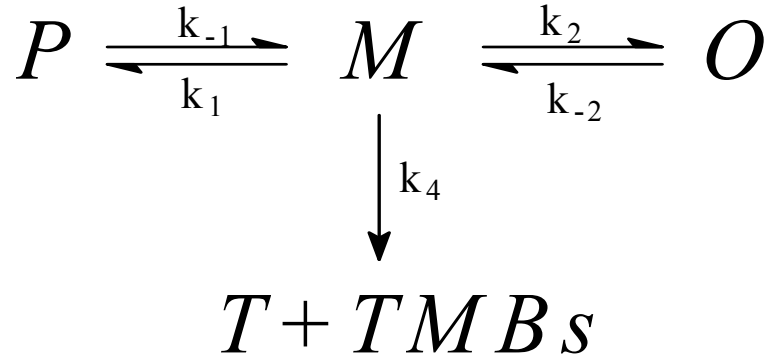
The increase in I/D ratio with partial coking deactivation can be easily explained based on the fact that disproportionation reaction is a bimolecular reaction and it will be enhanced as the number of active sites increases. Thus by pre-coking, some of the active sites are covered by coke, decreasing disproportionation selectivity which is more sites demanding than isomerization reaction. Furthermore, since in the case of ZSM-5, disproportionation reaction can take place only on the external sites, 1,3,5 TIPB can block these sites. Bauer et al [12] suggested that I/D ratio increases with pre-coking due to the reduction in strong external surface site number which is predominantly used for disproportionation reactions. Also it was noticed that pre-coking of ZSM-5 based catalyst have reduced both the o-xylene conversion and toluene and trimethylbenzene yields which are in agreement with the present result [7].

3.3 *P-xylene to o-xylene (P/O) ratio*

Kaeding and co-workers [3-6] suggested that an equilibrium mixture of xylene is formed as a primary product inside ZSM-5 pore structure. Thus a P/O ratio of about unity should be produced inside the pore structure of the present ZSM-5 based catalyst as a result of m-xylene isomerization. Fig. 6 depicts the effect of temperature and pre-coking on P/O ratio. In general, this ratio was found to decrease with temperature for both forms of the catalyst. However, P/O ratio was found to be less affected by m-xylene conversion. P/O ratio can be seen to decrease with temperature (at 10% m-xylene conversion, Fig.5) from 1.5 at 400°C to 1.2 at 500°C for the fresh catalyst. This suggests that as temperature increases the ratio of effective diffusivities of p- and o-xylene decreases and the produced p-xylene is converted via a secondary reaction such as disproportionation. As a result, it can be concluded that p-xylene selectivity is favored at lower than at higher temperatures. Another reason can be due to the bimolecular transmethylation mechanism which requires the reaction between 1,2,4 TMB and o-xylene molecules to form p-xylene and 1,2,4 TMB [14,37,38]. The present result suggested that the rate of this bimolecular reaction decreases with temperature leading to an increase in P/O ratio as reaction temperature decreases. A similar observation regarding a decrease in p-xylene selectivity at elevated temperature was reported by Vinek and Lercher [39] during the disproportionation of toluene over a ZSM-5 catalyst. Furthermore, the lower P/O ratio at higher temperature could also be explained by the secondary transformation of p-xylene through disproportionation and reversibly by isomerization to m-xylene at this temperature, which surpasses that of o-xylene, because of its higher reactivity. Fig 6 shows a comparison for total xylene yields between fresh catalyst and partially deactivated one. Between 400- 450°C and at 10 % m-xylene conversion, the deactivated catalyst has around 34% (xylenes yield) higher than the fresh one. However, this advantage decreased to about 15% at 500°C.

3.4 Kinetic Model Development

To develop a suitable kinetic model representing the overall transformation of m-xylene, the reaction network shown in Scheme 1 was proposed.



Scheme 1

The riser simulator mass balances based on the scheme 1 can be expressed as follows:
m-xylene (Scheme 1):

$$\frac{dy_m}{dt} = -[(k_1 + k_2 + k_4)y_m - \frac{k_1}{K_{pm}}y_p - \frac{k_2}{K_{om}}y_o] \frac{W_c}{V} \exp[-\alpha t] \quad (1)$$

$$\frac{dy_p}{dt} = [k_1y_m - \frac{k_1}{K_{pm}}y_p] \frac{W_c}{V} \exp[-\alpha t] \quad (2)$$

$$\frac{dy_o}{dt} = [k_2y_m - \frac{k_2}{K_{om}}y_o] \frac{W_c}{V} \exp[-\alpha t] \quad (3)$$

$$\frac{dy_d}{dt} = k_4y_m \frac{W_c}{V} \exp[-\alpha t] \quad (4)$$

The concentration of any species i in the above equations is related to its mass fraction as follows:

$$C_i = \frac{y_i W_{hc}}{MW_i V} \quad (5)$$

while the influence of temperature on the model parameters can be accounted for, through the following Arrhenius equation:

$$k_i = k_{0i} \exp\left(\frac{-E_i}{R} \left[\frac{1}{T} - \frac{1}{T_0}\right]\right) \quad (6)$$

T_0 is the average reaction temperature introduced to reduce parameters interaction of kinetic constants. As mentioned earlier, the time on stream" decay function ($\varphi = \exp[-\alpha t]$) is employed in the mathematical models to account for catalyst deactivation.

In order to ensure thermodynamic consistency at equilibrium, the rate constants for *m*- to *p*-xylene, and *m*- to *o*-xylene reactions in the above equations are expressed as follows [40,41]:

$$k_{-1} = k_1/K_{pm} \quad (7)$$

$$k_{-2} = k_2/K_{om} \quad (8)$$

where $K_{pm} = (C_p/C_m)_{eq}$ and $K_{mo} = (C_o/C_m)_{eq}$ are temperature-dependent equilibrium constants for both reactions, respectively. However, an average value can be computed for both constants, because the thermodynamic equilibrium concentrations of the xylenes remain fairly constant within the temperature range of this work. The xylene equilibrium concentrations are obtained from published works [37, 40, 41].

Each set of equation for the simplified models involves seven adjustable model parameters that have to be estimated before a solution is obtained. These parameters were adjusted using the weighted least-square algorithm for nonlinear parameters in a MATLAB package. The results obtained in this regard are presented and discussed in subsequent sections.

3.5 Modeling Results

The apparent kinetic parameters (k_0 , E , & α) were determined using non linear regression of the experimental data and are reported in Table 2 (for the fresh catalyst) with their corresponding 95% confidence limits. The values of the activation energies are generally lower than those reported by Li et. [42]. E_1 was found to be the smallest among all the activation energies followed by E_2 (*m*-xylene to

oxylene) and finally E_4 (activation energy of disproportionation). This indicates that the conversion of m-xylene to p-xylene is the easiest. The ratio of diffusion coefficients over HZSM-5 between p-,o-, and m-xylene was reported as $D_p = 100D_o = 1000D_M$ [11], and as $D_p = 1000D_o = 1000D_M$ [43], it is expected that $P/O > 1$. This means that the amount of p-xylene produced should exceed that of o-xylene because o-xylene might undergo further reaction before leaving the zeolite crystal [44]. *Based on the kinetic parameters in Table 2, k_1 and k_2 are calculated at 400 C. It has been found that $k_1 = 4.3 \times 10^{-5}$ and $k_2 = 3.5 \times 10^{-6} \text{ m}^3/(\text{kg cat. sec})$ which means that $k_1/k_2 = 12.3$. Bauer et al (28) reported that for the fresh catalyst this ratio was found to be close to 7. Hsu et al (45) reported k_1 parameters to be 268 as k_0 and $E_1 = 9.4 \text{ kcal/mol}$ while for k_2 to be 17.5 as k_0 and 7.1 kcal/mol as E_2 . Thus at 400C the ratio of $k_1/k_2 = 3$ despite the found $E_1 > E_2$.*

The results for the deactivated catalyst kinetic modelling are shown in Table 3. It can be seen from Table 3 that the apparent activation energy for the m-xylene isomerization to p-xylene has decreased by 35% to 2.28 kcal/mol. On the other hand the activation energy of m-xylene isomerization into o-xylene has increased by 32%. However, the major increase in activation energy was for the disproportionation reaction. Table 3 reports that the new activation energy was raised to 12.93 kcal/mol which corresponds to more than 77% increment from the value for the fresh catalyst (7.3 kcal/mol). These results substantiate that the pre-coking has increased the rate of p-xylene formation and decreased the rate of disproportionation reaction and leaving the formation rate of o-xylene essentially unchanged. Many researchers suggested that toluene is formed during m-xylene transformation via p-xylene disproportionation [44] and the present kinetic data indicate that p-xylene formation increases while disproportionation products decrease. Thus the partial catalyst deactivation has deactivated the external acid sites where the p-xylene (generated inside ZSM-5 pores) used to undergo disproportionation reaction leading to increase p-xylene formation rate and decreasing disproportionation reaction rate. It can be mentioned here that silylation can also enhance p-xylene selectivity but by a different mechanism. Silylation usually leads to narrowing of the pore opening and high p-xylene selectivity results due to the higher p-xylene diffusivity compared to that o- or m-xylene [46].

Based on the kinetic parameters in Table 3, k_1 and k_2 are calculated at 400 C. It has been found that $k_1 = 1.02 \times 10^{-4}$ and $k_2 = 4.25 \times 10^{-7} \text{ m}^3/(\text{kg cat. sec})$ which means that $k_1/k_2 = 240$. It is clear that k_1/k_2 ratio for the pre-coked catalyst is much larger than that for the fresh catalyst. It can be also noticed that k_1 for pre-coked catalyst is larger than that of the fresh catalyst by 2.4. However, k_2 for the fresh

*catalyst is found much larger than that of the pre-coked one which can conclude that k_2 is much affected by pre-coking than k_1 . Furthermore the increment in k_1 value with pre-coking can be explained by the fact that pre-coking increases the formation of *p*-xylene and decreases the formation of *o*-xylene by preventing the secondary transformation of *p*-xylene to *m*-xylene and other products. Bauer et al (28) reported that k_1/k_2 for the pre-coked catalyst is almost double that the fresh catalyst.*

3.6 Comparison between Experimental results and Model Predictions

To check the validity of the estimated kinetic parameters using with the overall kinetic model (Scheme 1), the fitted parameters were substituted into the model developed for this scheme, and the equations were solved numerically using the fourth order Runge-Kutta method. The simulated results were compared with the experimental data as shown in Figures 7 and 8. It can be observed from these figures that the simulated results compare fairly well with the experimental data. This provides significant evidence that the overall model could be used for the interpretation of the data obtained during *m*-xylene transformation for both fresh and pre-coked catalysts in the riser simulator.

In summary, the good agreement between the model and experimental results proves that the scheme 1 based on “time on stream” decay model can be used to successfully model the overall *m*-xylene transformation. This model shows the deactivation effect of the catalyst on the reaction kinetics.

3.7 Mass Transfer Effect

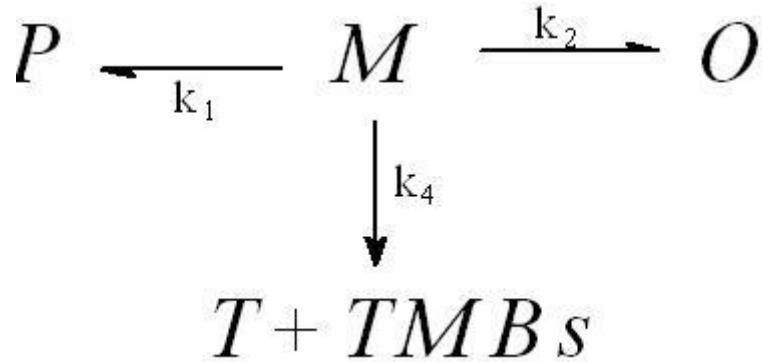
Al-Khattaf [47] recently studied the effect of mass transfer on xylene reaction over ZSM-5 based catalyst in the riser simulator. Since the riser simulator is a constant volume batch reactor unit, operated isothermally, a suitable material balance equation that describes reactant disappearance is given by Al-Khattaf and de Lasa [48] as:

$$-\frac{V}{W_c} \frac{dC_A}{dt} = \eta_{ss} r_A \varphi \quad (9)$$

where C_A is the reactant concentration in the riser simulator; V the volume of the reacting mixture (45 cm³); W_c the mass of the catalysts in the reacting system (0.81 gcat); η_{ss} an effectiveness factor to

account for the influence of the pore diffusion resistance on the overall reaction rate; φ is the intrinsic decay function that takes into account the deactivation of the catalyst; and r_A the reaction rate.

It is essential to note that the earlier study [47] was carried out based on the overall disappearing of reactant (xylenes) and no detailed kinetic modelling was given. However, the present kinetic model representing the overall transformation of *m*-xylene via isomerization and disproportionation reactions only and the mass transfer effect was included. Only irreversible reaction was considered to study the effect of diffusion (scheme 2). This assumption was validated by testing the irreversibly on the apparent kinetic parameters and comparing them with the reversible scheme (1). As shown in Tables 4&5 no much differences were found between the two kinetics sets. Thus based on these results, *m*-xylene isomerization is assumed as irreversible reaction. The short reaction times (3-15sec) is an important reason for the insignificant effect of the reversibility. The reaction equations are given by the following set of species balances and catalytic reactions (with the deactivation function described by time-on-stream):



Scheme 2

$$\frac{V}{W_c} \frac{dC_{m\text{-xylene}}}{dt} = -[\eta_1 k_1 C_{m\text{-xylene}} + \eta_2 k_2 C_{m\text{-xylene}} + 2\eta_4 k_4 C_{m\text{-xylene}}^2] \exp[-\alpha t] \quad (10)$$

$$\frac{V}{W_c} \frac{dC_{p\text{-xylene}}}{dt} = \eta_1 k_1 C_{m\text{-xylene}} \exp[-\alpha t] \quad (11)$$

$$\frac{V}{W_c} \frac{dC_{o\text{-xylene}}}{dt} = \eta_2 k_2 C_{m\text{-xylene}} \exp[-\alpha t] \quad (12)$$

$$\frac{V}{W_c} \frac{dC_{toluene}}{dt} = \eta_4 k_4 C_{m-xylene}^2 \exp[-\alpha t] \quad (13)$$

Where η_i are the effectiveness factors; k_i , intrinsic rate constants ($\text{cm}^3/\text{gcat}\cdot\text{sec}$); α is a deactivation constant and t is the time the catalyst is exposed to a reactant atmosphere (time-on-stream [TOS]).

It should be noted that the following assumptions were made in deriving the reaction network:

1. The isomerization of *m*-xylene follows simple first-order, whereas disproportionation is second order as proposed by Atias *et al.* [49] and Ko and Kuo[50]
2. An irreversible reaction path is assumed for both the isomerization and disproportionation reaction.
3. Trimethylbenzenes are entirely the results of the disproportionation reaction. [The disproportionation reaction involves the formation of 1 mole of Toluene and 1 mole of trimethylbenzenes from 2 moles of *m*-xylene]
4. The model assumes catalytic reactions only and neglects thermal conversion. This hypothesis of a negligible contribution from thermal reactions has been fully justified [30].
5. A single deactivation function defined for all the reactions taking place.
6. The reactor operates under isothermal conditions, justified by the negligible temperature change observed during the reactions.

Using similar derivation procedures outlined in Atias *et al.* [49], eqs 10-13 can be expressed in terms of weight fractions which are the measurable variables from GC analysis as:

$$\frac{dy_A}{dt} = -[\eta_1 k_1 y_A + \eta_2 k_2 y_A + 2\eta_4 v_A k_4 y_A^2] \frac{W_c}{V} \exp[-\alpha t] \quad (14)$$

$$\frac{dy_B}{dt} = \eta_1 k_1 y_A \frac{W_c}{V} \exp[-\alpha t] \quad (15)$$

$$\frac{dy_C}{dt} = \eta_2 k_2 y_A \frac{W_c}{V} \exp[-\alpha t] \quad (16)$$

$$\frac{dy_D}{dt} = v_i \eta_4 k_4 y_A^2 \frac{W_c}{V} \exp[-\alpha t] \quad (17)$$

where A, B, C and D represent *m*-xylene, *p*-xylene, *o*-xylene, and the disproportionation product represented by toluene, respectively. And,

$$v_A = \frac{W_{hc}}{MW_{m-xylene} V} \quad v_t = \frac{W_{hc} MW_{toluene}}{MW_{xylene}^2 V}$$

where

W_{hc} = total mass of hydrocarbons inside the riser (0.162 g)

MW_X = molecular weight of X molecule

Kinetic constants for isomerization and disproportionation can be expressed using the Arrhenius equation, and a centering temperature, T_o is the average reaction temperature introduced to reduce parameter interaction.

$$k_i = k_{0i} \exp\left(\frac{-E_i}{R} \left[\frac{1}{T} - \frac{1}{T_o}\right]\right) \quad (18)$$

The effectiveness factor (η_{ss}) expresses the extent of diffusional constraints inside a catalyst. For a zeolite crystal under steady state, η_{ss} is defined as the ratio of the actual reaction rate to the reaction rate in the absence of internal diffusional resistance.

$$\eta_{ss} \approx \frac{\tanh(h')}{h'} \quad (19)$$

Where h' is the modified Thiele Modulus, defined as;

$$h' = \frac{1}{a_{ext}} \sqrt{\frac{(n+1) k_{A,in} \rho_{cr} \phi_{in} C_i^{n-1}}{2 D_{eff}}} \quad (20)$$

with a_{ext} being the specific external surface area for the zeolite crystal ($a_{ext}=6/D_{cr}$); n the reaction order; C_i^{n-1} bulk concentration; D_{eff} the effective diffusivity, and ρ_{cr} is the zeolite density (825 kg/m³).

The effective diffusivity coefficient in zeolites can be represented as:

$$D_{eff} = D_0 \exp\left(-\frac{E_D}{RT}\right) \quad (20)$$

where E_D represents the diffusion activation energy.

Eq 20 is very useful in estimating temperature effect on reactant transport. Based on the experimental results reported by Choudhary et al. [51] for *m*-xylene diffusivity over ZSM-5, energy of activation of 9.0 kcal/mol and $D_O = 5.8 \times 10^{-13} \text{ m}^2/\text{s}$ were estimated by the authors. Thus, the above reported E_D and D_O values will be employed in calculation of the effectiveness factor (η_{ss}).

Therefore, catalytic conversion of *m*-xylene in the riser simulator can be modeled using a set of equations, namely, eqs 14-17. Since the diffusion parameters (D_O and E_D) are known, only seven intrinsic kinetic parameters $k_1 (k'_0, E_R)$, $k_2 (k'_0, E_R)$, $k_4 (k'_0, E_R)$ and α need to be determined to fully characterize the diffusive- reactive system.

The intrinsic kinetic parameters for k_1 , k_2 and k_4 (k_0 , E) & α were determined using non linear regression of the experimental data and are reported in Table 6 (for the fresh catalyst). The values of the activation energies are generally lower than the apparent parameters reported in Tables 2-5. However, the same trend was noticed for intrinsic parameters as apparent parameters. E_1 was found to be the smallest among all the activation energies followed by E_2 (m-xylene to o-xylene) and finally E_4 (activation energy of disproportionation).

The results for the deactivated catalyst kinetic modelling are shown in Table 7. It can be seen from Table 7 that the intrinsic activation energy for the m-xylene isomerization to p-xylene is around 2 kcal/mol. On the other hand the activation energy of m-xylene isomerization into o-xylene has increased by more than 100%. Furthermore the activation energy for the disproportionation reaction was increased by 73%.

Now according to Levenspiel [52] the apparent activation energy E_{APP} is equivalent to half of the summation of the intrinsic activation energy E_{in} and the diffusion activation energy E_D as follows;

$$E_{APP} = \frac{E_{in} + E_D}{2} \quad (21)$$

Hence based on Eq (21), where E_D is equal to 9 kcal/mol and from Table 6 E_{in} for disproportionation reaction is equal to 6 kcal/mol, the apparent activation energy for the disproportionation reaction = $(6+9)/2 = 7.5$ kcal/mol and for o-xylene formation = $(2.87+9)/2 = 6$ kcal/mol. These values match very well with the apparent activation energy for the two reactions which was reported in Table 4. However, for p-xylene formation the situation is more complicated where the apparent activation energy = $(1.68 + 9)/2 = 5.3$ kcal/mol. But in Table 4 a value of 3.1 kcal/mol was found.

The Thiele Modulus and effectiveness factors for the reactions (m-xylene isomerization to p-xylene, m-xylene isomerization to o-xylene and the disproportionation reactions) are calculated based on the intrinsic kinetic parameters. Table 8 reports the effectiveness factors for the fresh catalyst. It is clear that the reaction is controlled by strong mass transfer limitation for all the reaction pathways. For the fresh catalyst, the effectiveness factor is bounded between 0.1 and 0.25. The effectiveness factors generally increases with both reaction temperature and reaction time. For the pre-coked catalyst, the effectiveness factor was found to be between 0.1 and 0.3 which indicates that the reaction is also

hindered with mass transfer. The different effectiveness factor for the pre-coked catalyst along with Thiele Modulus are reported in Table 9.

Conclusions

The following conclusions can be drawn from transformations of m-xylene over fresh and pre-coked ZSM-5 in the riser simulator under the conditions of the present study:

1. The pre-coking has affected both the reactivity of m-xylene and the selectivity. While the m-xylene conversion has decreased with pre-coking, isomerization reaction selectivity has immensely increased. The higher value of this ratio with pre-coking was explained by the deactivation of the external active sites which increased the difficulty of accommodating two molecules of xylene, necessary for disproportionation. The difference in I/D ratio between the fresh and the pre-coked catalysts was maximum at 400C and it reached around 6. However, this difference was found to decrease rapidly with temperature reaching a minimum (less than 1) at 500C.
2. For both catalysts P/O ratio was more than 1 and this is expected since ZSM-5 is the origin of both catalysts. P/O ratio was always higher for the pre-coked catalyst and it was found to decrease with temperature for both catalysts. The maximum P/O ratio was obtained at 400C for the pre-coked catalyst (> 2.5).
3. It is evident that the partial coking has decreased the secondary conversion of the produced p-xylene. This suggested that the disproportionation reaction was taken place on both the matrix and the external zeolite active sites. The modeling results support this argument since the apparent activation energy of the p-xylene formation over the pre-coked catalyst has decreased by 32%, the apparent activation energy of the o-xylene formation has increased by 40% and the apparent activation energy of the disproportionation reaction has increased by 75%.
4. It can be concluded that m-xylene reaction over ZSM-5 based catalyst is severely hindered by reactant diffusion.

Acknowledgment

The author gratefully acknowledges King Fahd University of Petroleum & Minerals for the financial support provided for this work. I would like also to thank Mr. Mariano Gica for his useful collaboration on the experimental work.

References

- [1] N. Y. Chen, *Ind. Eng. Chem. Res.* 40(2001) 4157.
- [2] N. Y. Chen, *J. Catal.* 17(1988) 114.
- [3] N. Y. Chen, W. W. Kaeding and F. G. Dwyer, *J. Am. Chem. Soc.*, 101 (1979) 6783.
- [4] W. W. Kaeding, C. Chu, L. B. Weinstein and S.A Butter, *J. Catal.* 67 (1981) 159.
- [5] W. W. Kaeding, C. Chu, L. B. Weinstein and S.A Butter, *J. Catal.* 69 (1981) 392.
- [6] L. B. Young, S. A. Butter and W. W. Kaeding, *J. Catal.* 76 (1982) 418.
- [7] F. Bauer, W. Chen, Q. Zhao, A. Freyer, and S. Liu, *Microporous and Mesoporous Materials* 47 (2001) 67.
- [8] V. Mavrodinova and M. Popova, *Catalysis Communication* 6 (2005) 247.
- [9] Y.S. Bhat, J.Das, K.V. Rao and A.B. Halgeri, *J. Catal.* 159 (1996) 368.
- [10] H. Vinek and J. A. Lercher, *J. Mol. Catal.* 64 (1991) 23.
- [11] G. Mirth, J. Cejka and J. A. Lercher, *J. Catal.* 139 (1993) 24.
- [12] F. Bauer, E. Bilz, and A. Freyer, *Appl. Catal. A: Gen*, 289 (2005) 2.
- [13] U. Kurschner, B. Parltitz, E. Schreier, G. Ohlmann and J. Volter, *Appl. Catal. A: Gen*, 30 (1987) 159.
- [14] J. C. Vedrine, A. Auroux, P. Dejaifve, V. Ducarme, H. Hoser and S. Zhou, *J. Catal.* 73 (1982) 147.
- [15] H. Vinek, G. Rimplmayr and J. A. Lercher, *J. Catal.* 115 (1989) 291.
- [16] Y. Li and H. Yu, *Appl. Catal. A: Gen*, 142 (1996) 123.
- [17] P. Ratnasamy and S. K. Pokhriyal, *Appl. Catal. A: Gen*, 55 (1989) 265.
- [18] K. Beschmann and L. Riekert, *J. Catal.* 141 (1993) 548

- [19] U. Kurschner, H. G. Jerschke, E. Schreier and J. Volter, *Appl. Catal. A: Gen*, 57 (1990) 167.
- [20] *U. S. Pat. 4 358 395* (1982) to W.O. Haag, D. H. Olson and P. G. Rodewald.
- [21] *U. S. Pat. 4 508 836* (1985) to W.O. Haag, D. H. Olson and P. G. Rodewald.
- [22] F. T. Starzyk, A. Vimont and J. Gilson, *Catalysis Today*, 70 (2001) 227.
- [23] C. W. Jones, S. I. Zones and M. E. Davis, *Appl. Catal. A: Gen*, 181 (1999) 289.
- [24] T. Tsai, S. Liu and I. Wang, *Appl. Catal. A: Gen.*, 181 (1999) 355.
- [25] S. Al-Khattaf, *Ind. Eng. Chem. Res.*, 1(2007)59.
- [26] D. H. Olson and W. O. Haag, in *Catalytic materials*, T. E. Whyte et al. (eds.), ACS Symp. Ser. 248, Am. Chem. Soc., Washington D.C., (1984) 275.
- [27] M. Niwa, S.Kato, T.Hattori and Y.Mrakami, *J.Chem. Soc. Faraday Trans*, 80(1984)3135.
- [28] F. Bauer, W. Chen, H. Ernst, S. Haung, A. Freyer, and S. Liu, *Microporous and Mesoporous Materials* 72 (2004) 81.
- [29] *U.S. Pat. 5 102 628* (1992) to H.I. de Lasa.
- [30] D. W. Kraemer, Ph.D. Dissertation, University of Western Ont., London, Canada 1991.
- [31] A. Iliyas and S.Al-Khattaf, *Ind. Eng. Chem. Res.*, 43 (2004) 1349.
- [32] A. Iliyas and S. Al-Khattaf, *Applied Catalysis A*, 269 (2004)225.
- [33] S. Al-Khattaf, N. Tukur, A. Al-Amer, *Ind. Eng. Chem. Res.*, 44(2005)7957.
- [34] S. Morin, P. Ayrault, S. El Mouahid, N.S. Gnep and M. Guisnet, *Appl. Catal. A: Gen*, 159 (1997) 317.
- [35] A. Corma, E.Sastre, *J. Catal.* 129 (1991) 177.
- [36] S. Morin, N.S. Gnep and M. Guisnet, *Appl. Catal. A: Gen*, 168 (1998) 63.
- [37] J. Cejka and B. Wichterlova, *Catal.Rev.* 44 (2002) 375.
- [38] S. Morin, P. Ayrault, N.S. Gnep and M. Guisnet, *Appl. Catal. A: Gen*, 166 (1998) 281.
- [39] H. Vinek and J. A. Lercher, *J. Mol. Catal.* 64 (1991) 23.
- [40] Gendy, T. S. *J. Chem. Technol. Biotechnol.*, 73 (1998) 109.
- [41] Stull, D. R., Westrum, E. F., Simke, G. C. *The Chemical Thermodynamics of*

Organic Compounds, Wiley, New York, (1969)368.

[42] Y. Li, X. Chang, and Z. Zeng, *Ind. Eng. Chem. Res.* 31 (1992)187.

[43] S. Zheng, A. Jentys and J. A. Lercher, *J. Catal.* 219 (2003) 310.

[44] J. Wei, *J. Catal.* 76 (1982) 433.

[45] Y.S. Hsu, T.Y. Lee, and H.C. Hu, *Ind. Eng. Chem. Res.* **1988**, 27, 942-947.

[46] S. Zheng, A. Jentys and J. A. Lercher, *J. Catal.* 241 (2006) 304.

[47] S.Al-Khattaf, *Ind. Eng. Chem. Res.*, 46(1) (2007) 59

[48] S. Al-Khattaf, and H. de Lasa, *The Canadian Journal of Chgematical Engineering*, 2001, 79, 341-348.

[49] J. A., Atias, G. Tonetto, and H. de Lasa,, *Ind. Eng. Chem. Res.* **2003**, 42, 4162-4173.

[50] A. Ko,; C. T., Kuo,. *J. Chin. Chem. Soc.* **1994**, 41, 141-150.

[51] V.R. Choudhary, V. S.; Nayak,; T. V, Choudhary,. *Ind. Eng. Chem.Res.* **1997**, 36, 1812-1818.

[52] O. Levenspiel “ Chemical Reaction Engineering” Third Edition, John Wiley & Sons, 1999.

Table 1: Catalyst Characterization

Catalyst	Surface Area (m ² /g)	Na ₂ O %	Acidity (mmole/g)	% of weak acid site	% of strong acid site
Fresh	70	negligible	0.23	62.5	37.5
Pre-coked	63	negligible	0.18	66.67	33.33

Table 2: Estimated kinetic parameters for *m*-Xylene transformation based on Time on Stream (TOS Model) – **Fresh Catalyst**

Parameters	k_1 (isomerization to <i>p</i> -xylene)	k_2 (isomerization to <i>o</i> -xylene)	k_4 (disproportionation to toluene)
E_i (kcal/mol)	3.49	6.44	7.30
95% CFL	1.79	2.71	1.57
k_{0i}^a (m ³ /kg of catalyst.s)	0.47	0.30	0.01
95% CFL	0.05	0.04	0.001
α (1/sec) = 0.02 (95% CFL of 0.01)			

Table 3: Estimated kinetic parameters for *m*-Xylene transformation based on Time on Stream (TOS Model) – **Pre-coked Catalyst**

Parameters	k_1 (isomerization to <i>p</i> -xylene)	k_2 (isomerization to <i>o</i> -xylene)	k_4 (disproportionation to toluene)
E_i (kcal/mol)	2.28	8.53	12.92
95% CFL	1.40	2.88	3.00
k_{0i}^a (m ³ /kg of catalyst.s)	0.52	0.25	0.01
95% CFL	0.05	0.04	0.001
α (1/sec) = 0.04 (95% CFL of 0.02)			

^aPreexponential factor in the scaled equation

Table 4: (**Apparent & Irreversible**) Estimated kinetic parameters for *m*-Xylene transformation based on Time on Stream (TOS Model) – **Fresh Catalyst**

Parameters	k_1 (isomerization to <i>p</i> -xylene)	k_2 (isomerization to <i>o</i> -xylene)	k_4 (disproportionation to toluene)
E_i (kcal/mol)	3.07	6.00	7.35
95% CFL	1.62	2.34	1.52
$k_{0i}^a \times 10^3$ (m ³ /kg of catalyst.s)	0.42	0.30	0.013
95% CFL	0.04	0.03	0.001
α (1/sec) = 0.022 (95% CFL of 0.013)			

Table 5: (**Apparent & Irreversible**) Estimated kinetic parameters for *m*-Xylene transformation based on Time on Stream (TOS Model) – **Pre-coked Catalyst**

Parameters	k_1 (isomerization to <i>p</i> -xylene)	k_2 (isomerization to <i>o</i> -xylene)	k_4 (disproportionation to toluene)
E_i (kcal/mol)	2.01	8.47	12.86
95% CFL	1.18	2.56	2.69
$k_{0i}^a \times 10^3$ (m ³ /kg of catalyst.s)	0.45	0.23	0.006
95% CFL	0.04	0.03	0.001
α (1/sec) = 0.035 (95% CFL of 0.015)			

^aPreexponential factor in the scaled equation

Table 6: (**Intrinsic & Irreversible**) Estimated kinetic parameters for *m*-Xylene transformation based on Time on Stream (TOS Model) – **Fresh Catalyst**

Parameters	k_1 (isomerization to <i>p</i> -xylene)	k_2 (isomerization to <i>o</i> -xylene)	k_4 (disproportionation to toluene)
E_i (kcal/mol)	1.68	2.87	6.02
$k_{0i}^a \times 10^3$ (m ³ /kg of catalyst.s)	4.05	1.65	0.13
α (1/sec) = 0.036			

Table 7: (**Intrinsic & Irreversible**) Estimated kinetic parameters for *m*-Xylene transformation based on Time on Stream (TOS Model) – **Pre-coked Catalyst** (Diffusivity 95% of the fresh catalyst)

Parameters	k_1 (isomerization to <i>p</i> -xylene)	k_2 (isomerization to <i>o</i> -xylene)	k_4 (disproportionation to toluene)
E_i (kcal/mol)	2.21	7.44	10.40
$k_{0i}^a \times 10^3$ (m ³ /kg of catalyst.s)	3.83	1.13	0.035
α (1/sec) = 0.053			

^aPreexponential factor in the scaled equation

Table 8: Effectiveness factor and Thiele Modulus for *m*-xylene over ZSM-5 ($L = 1.0 \mu\text{m}$)
(*Fresh Catalyst*)

Temperature (oC)/Time (s)	Conversion (%)	h'_1	η_1	h'_2	η_2	h'_4	η_4
400							
3	4.9	10.501	0.0952	6.499	0.1539	11.027	0.0907
5	8.8	10.129	0.0987	6.270	0.1595	10.417	0.0960
7	10.1	9.771	0.1023	6.048	0.1653	9.976	0.1002
10	12.3	9.258	0.1080	5.730	0.1745	9.336	0.1071
13	16.3	8.771	0.1140	5.429	0.1842	8.641	0.1157
15	21	8.461	0.1182	5.237	0.1909	8.098	0.1235
450							
3	7.8	8.690	0.1151	5.547	0.1803	10.052	0.0995
5	10	8.383	0.1193	5.351	0.1869	9.581	0.1044
7	13	8.086	0.1237	5.161	0.1937	9.086	0.1101
10	21	7.661	0.1305	4.890	0.2045	8.203	0.1219
13	25	7.258	0.1378	4.633	0.2158	7.573	0.1321
15	26.6	7.002	0.1428	4.469	0.2237	7.227	0.1384
500							
3	9	7.370	0.1357	4.832	0.2069	9.339	0.1071
5	12	7.109	0.1407	4.661	0.2145	8.859	0.1129
7	18	6.858	0.1458	4.496	0.2224	8.249	0.1212
10	24	6.497	0.1539	4.260	0.2347	7.524	0.1329
13	28.1	6.156	0.1624	4.036	0.2476	6.934	0.1442
15	30.8	5.938	0.1684	3.893	0.2567	6.562	0.1524

Table 9: Effectiveness factor and Thiele Modulus for *m*-xylene over ZSM-5 ($L = 1.0 \mu\text{m}$)
(*Precoked Catalyst*)

Temperature (oC)/Time (s)	Conversion (%)	h'_1	η_1	h'_2	η_2	h'_4	η_4
400							
5	5.6	9.382	0.1066	4.452	0.2246	4.706	0.2125
7	6.8	8.925	0.1120	4.234	0.2361	4.434	0.2254
10	9.1	8.280	0.1208	3.929	0.2544	4.045	0.2471
13	11.5	7.682	0.1302	3.645	0.2740	3.686	0.2710
15	12.2	7.307	0.1369	3.467	0.2879	3.482	0.2867
450							
5	7.8	7.871	0.1270	4.276	0.2338	4.822	0.2074
7	9.0	7.488	0.1336	4.067	0.2457	4.543	0.2201
10	13.6	6.947	0.1440	3.773	0.2647	4.089	0.2444
13	14.7	6.445	0.1552	3.501	0.2851	3.752	0.2662
15	18.7	6.130	0.1631	3.330	0.2995	3.474	0.2873
500							
5	10.5	6.756	0.1480	4.128	0.2421	4.903	0.2039
7	12.4	6.426	0.1556	3.927	0.2545	4.600	0.2173
10	18.8	5.962	0.1677	3.643	0.2741	4.091	0.2443
13	20.5	5.531	0.1808	3.380	0.2952	3.738	0.2672
15	24.6	5.261	0.1901	3.215	0.3100	3.453	0.2890

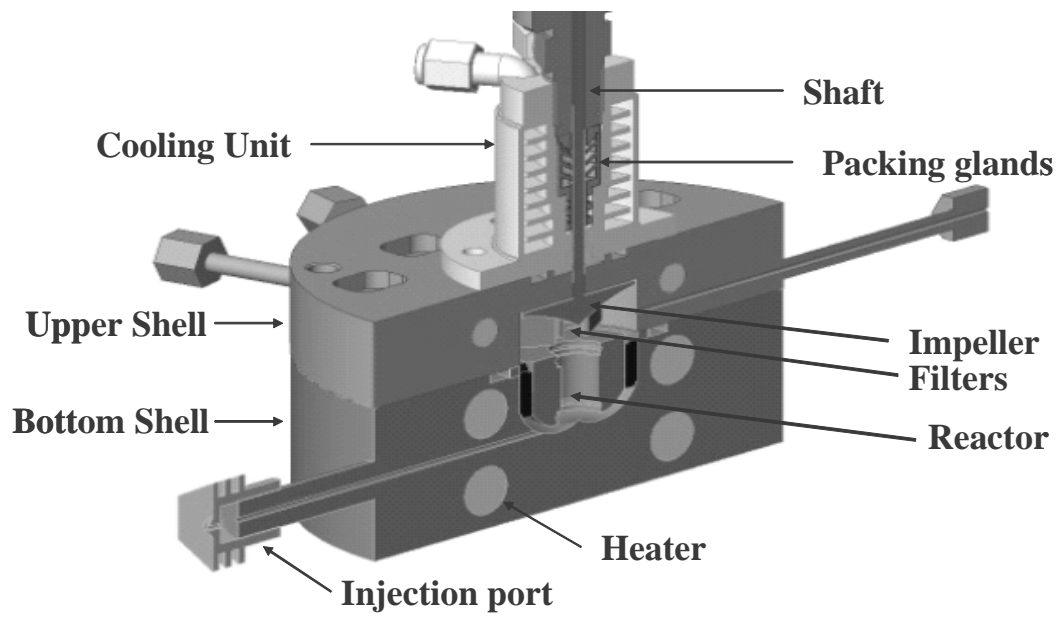


Fig. 1. Schematic diagram of the riser simulator

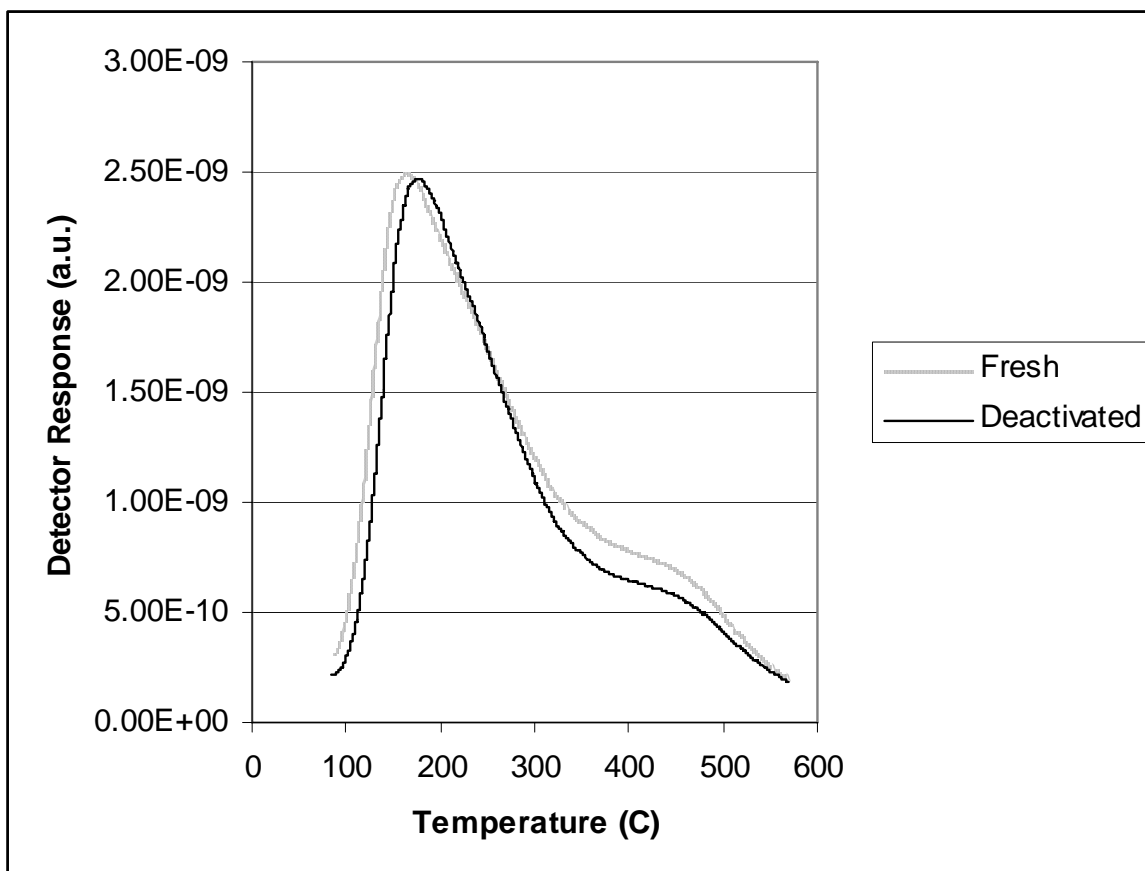


Fig 2: Ammonia desorption (TPD)

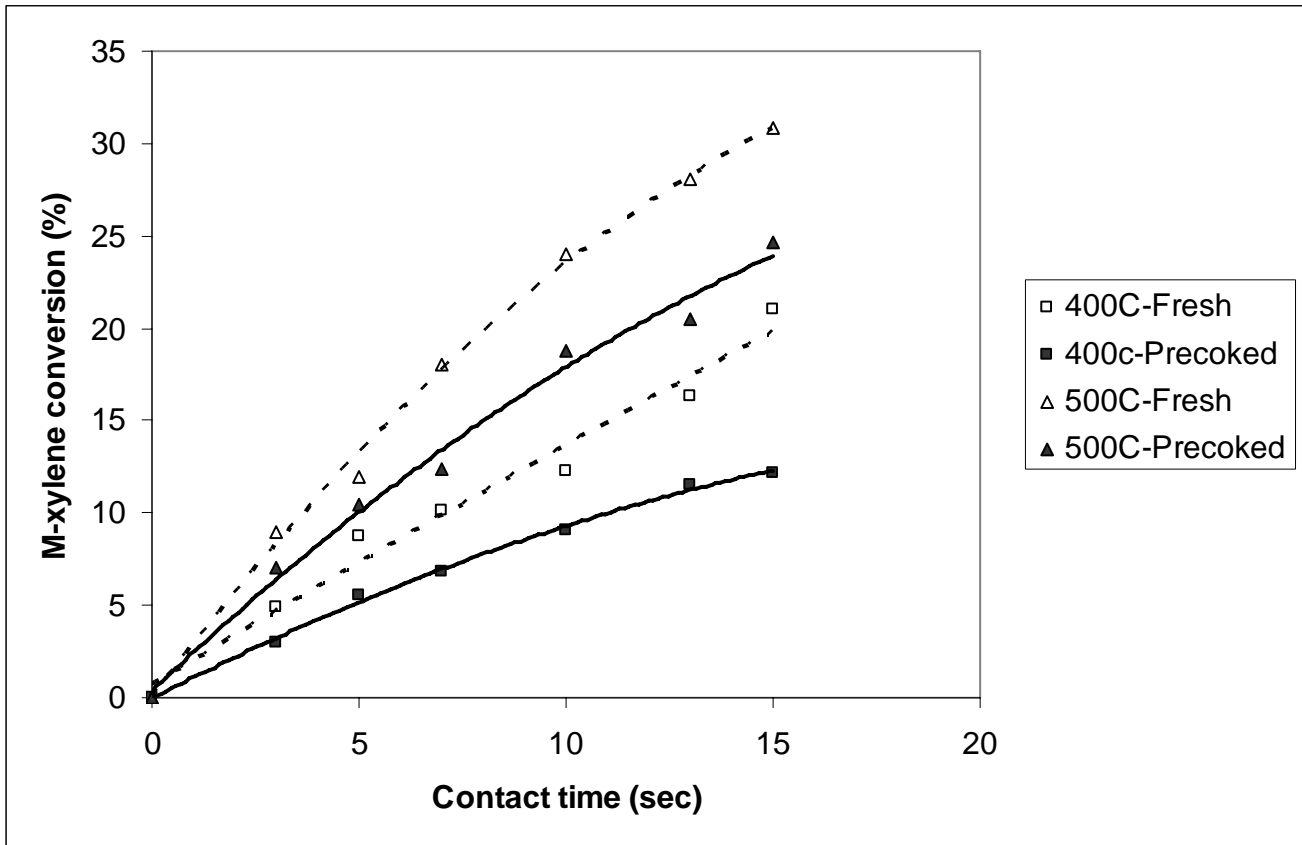


Fig 3. The Effect of reaction time and temperature on m-xylene conversion.

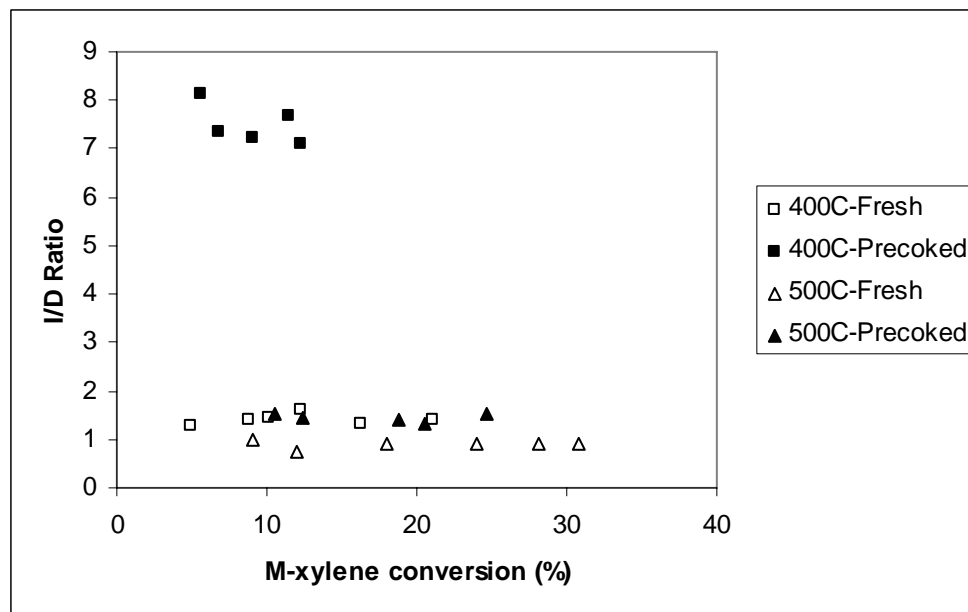


Fig. 4. The effect of m-xylene conversion, catalyst pre-coking and reaction temperature on I/D ratio.

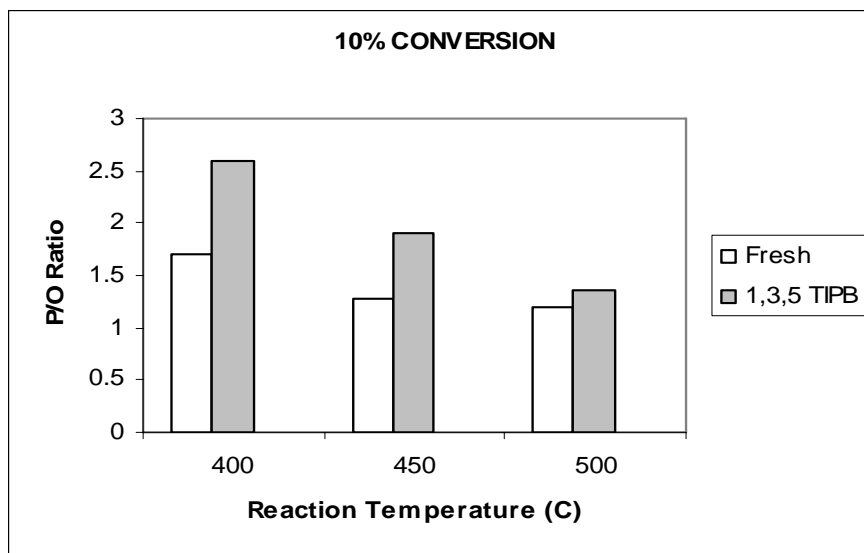


Fig. 5. The effect of catalyst pre-coking on P/O ratio at 10% m-xylene conversion.

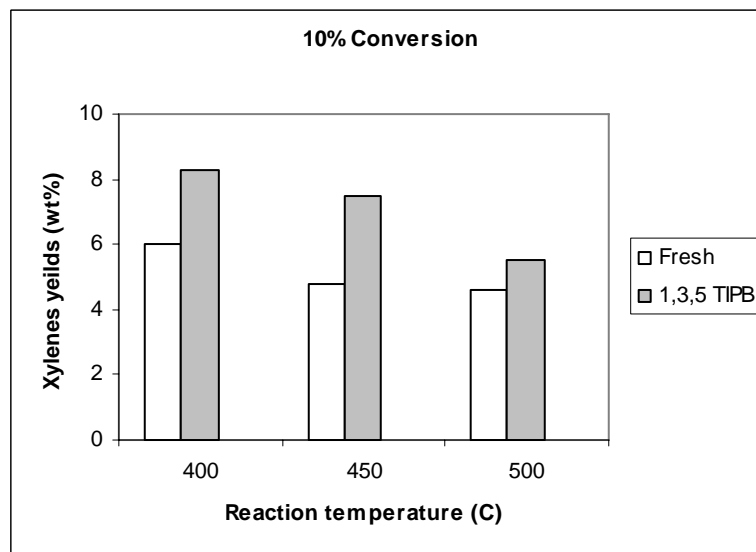


Fig. 6. The effect of catalyst pre-coking on total xylene yields at 10% m-xylene conversion.

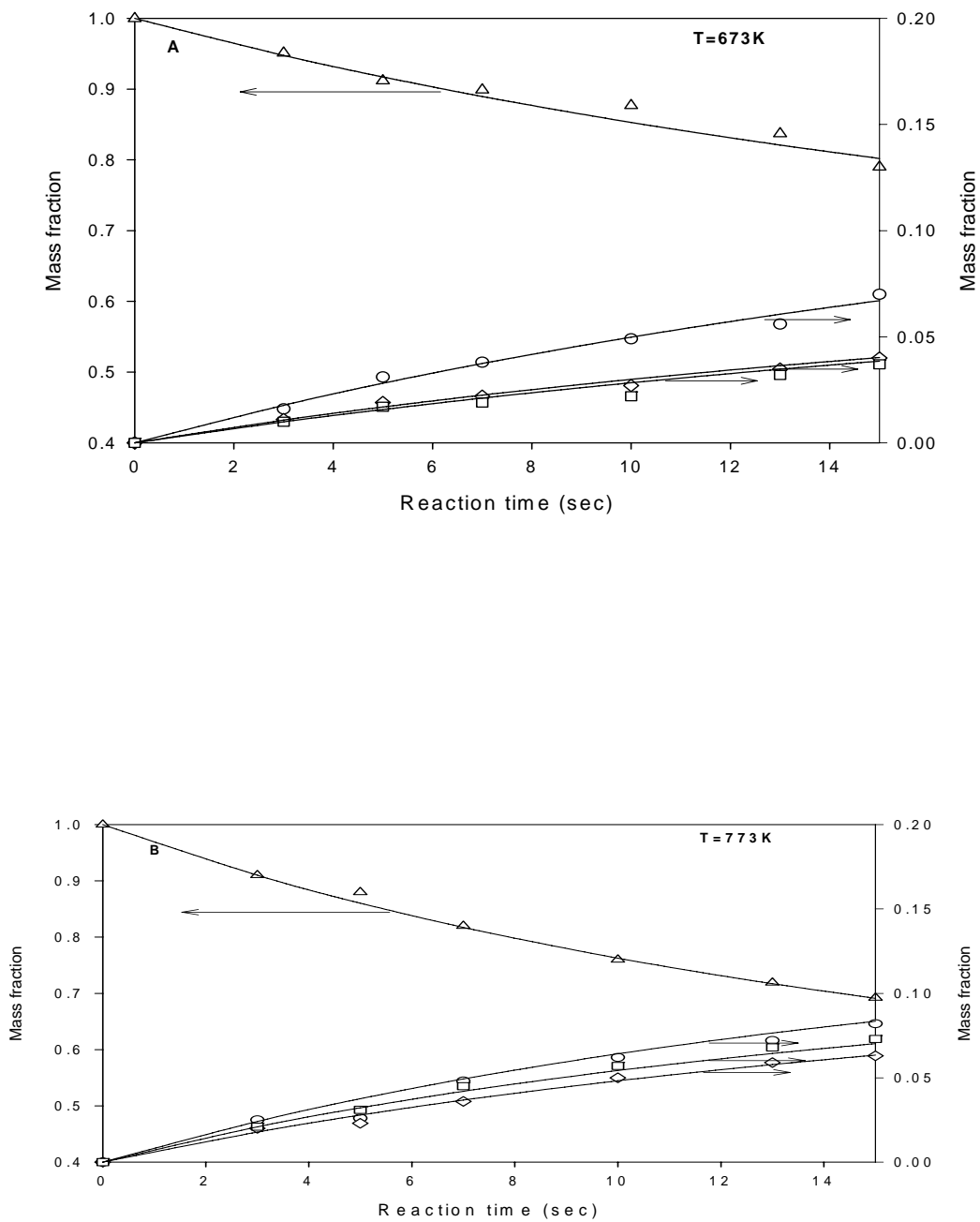


Figure 7: Comparison between experimental results and numerical simulations (—) of *m*-xylene transformation over Fresh catalyst (**Apparent & Reversible**) (A) $T = 673$ K; (B) $T = 773$ K; (○) *p*-xylene yields; (□) Toluene yields; (◇) *o*-xylene yields; (Δ) *m*-xylene yields

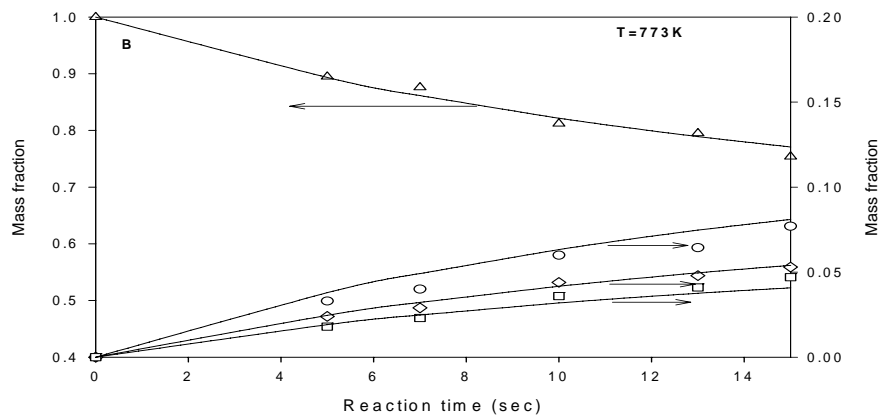
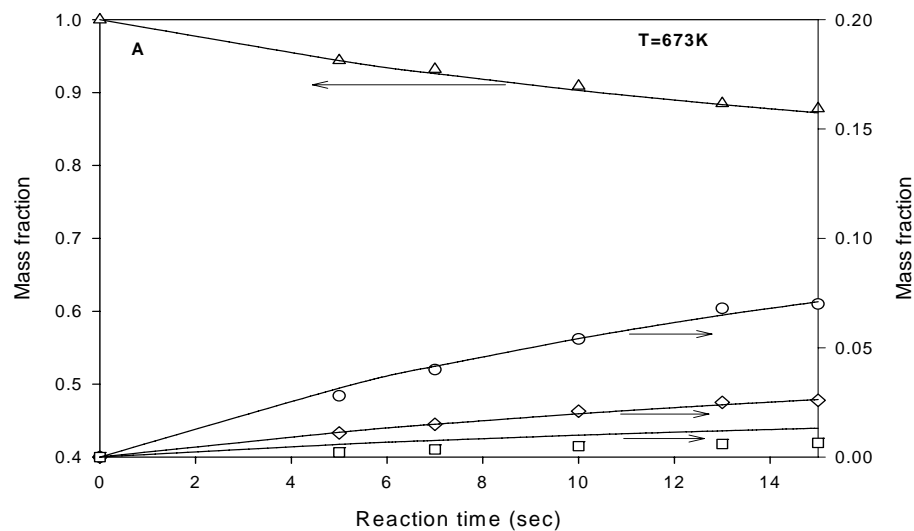


Figure 8: Comparison between experimental results and numerical simulations (—) of *m*-xylene transformation over Precoked catalyst (**Apparent & Reversible**) (A) $T = 673\text{ K}$: (B) $T = 773\text{ K}$: (○) *p*-xylene yields; (□) Toluene yields; (◇) *o*-xylene yields; (Δ) *m*-xylene yields