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Gas-phase isomerization of *meta*-xylene over USY zeolite in a Riser Simulator: a simplified kinetic model

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Abstract

The gas-phase isomerization of *meta*-xylene has been carried out over USY zeolite catalyst using a fluidized bed reactor under relevant reaction conditions for FCC (temperature, contact time, reactant partial pressure, catalyst/oil ratio). Experimental results clearly indicate the presence of bimolecular isomerization pathway, in addition to the monomolecular isomerization reaction. The disproportionation/isomerization (D/I) ratio was found to increase steadily with both *m*-xylene conversion and reaction temperature, whereas *p*-xylene/*o*-xylene (P/O) ratio was only mildly affected with both reaction parameters. A simplified kinetic model based on reactant-converted (RC) deactivation model was developed for the reaction and compared with the obtained experimental data. The apparent kinetic parameters were estimated using nonlinear regression analysis.

Keywords: *Meta*-xylene isomerization; Fluidized bed reactor; USY zeolite; Kinetic modeling

1. Introduction

The catalytic isomerization of *meta*-xylene has gained considerable interest over the years. This is evident from the volume of papers published in this regard [1–14]. Consequently, rapid developments were recorded in this field in recent times resulting in commercialization of several novel processes for the reaction. In most of the literatures, fixed bed reactors are often employed for the reaction. However, temperature and concentration gradients have been reported to pose difficulties in obtaining accurate experimental data from such studies [1].

In this work, the Riser Simulator which is operated as a batch, well-mixed, fluidized bed reactor will be used as tool in investigating xylene isomerization over USY zeolite catalyst. Employing this type of reactor can reduce the problems of temperature and concentration gradients associated with fixed bed reactors. Moreover, to our knowledge, this reaction has not been reported in the open literature to have been carried out in such a reactor. USY zeolite has been chosen since it serves as a standard FCC catalyst, besides only a few studies reporting the kinetic parameters for the various reaction paths during *m*-xylene isomerization reaction over USY zeolite is available [3].

The aim of this study is to investigate the kinetics of gas-phase isomerization of *meta*-xylene over USY zeolite catalyst in a fluidized bed reactor under low *meta*-xylene conversion levels. In addition, a simplified kinetic model which describes the reaction under the present conditions will be developed. The proposed model will be tested with the obtained experimental data and the model parameters estimated using nonlinear regression analysis.

2. Experimental

All the experimental runs were carried out in the Riser Simulator. This reactor is a novel bench-scale equipment with internal recycle unit invented by de Lasa [15] to overcome the technical problems of the standard micro-activity test (MAT), and it is fast becoming a valuable experimental tool for reaction evaluation involving model compounds [16–18], and also for testing and developing new FCC in VGO cracking [19,20]. A schematic diagram of the Riser Simulator is shown in Fig. 1. A detailed description of various Riser Simulator

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Nomenclature

C_i	gas-phase concentration of species i (kmol/m^3)
CFL	confidence limit
D	disproportionation reaction
E_i	apparent activation energy for the ith reaction (kJ/mol)
I	isomerization reaction
k_i	apparent rate constant for the ith reaction (m^3/kg$_{\text{cat}}$ s)
k_{oi}	pre-exponential factor for the ith reaction (m^3/kg$_{\text{cat}}$ s)
M	*meta*-xylene
MW$_i$	molecular weight of species i (kg/kmol)
O	*ortho*-xylene
P	*para*-xylene
r	correlation coefficient
R	universal gas constant (kJ/kmol K)
t	reaction time (s)
T	toluene
T_0	average temperature of the experiment
TMBs	trimethylbenzenes
V	Riser Simulator volume (50×10^6 m^{-3})
W_c	catalyst mass (kg$_{\text{cat}}$)
W_{hc}	mass of hydrocarbon injected into the Riser Simulator (0.16×10^{-3} kg)
y_d	mass fraction of disproportionation products
y_m	mass fraction of *meta*-xylene
y_o	mass fraction of *ortho*-xylene
y_p	mass fraction of *para*-xylene

Greek letters

φ	apparent deactivation function
λ	catalyst deactivation constant

components, sequence of injection and sampling can be found in Kraemer [21].

Ultrastable 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 and was calcined for 2 h at 600 °C and steamed at 760 °C for 5 h. Table 1 reports the catalyst main properties following catalyst pretreatment. The reaction products were analyzed in an Agilent 6890N gas chromatograph with an FID detector and a capillary column INNOWAX, 60 m cross-linked methyl silicone with an internal diameter of 0.32 mm.

Table 1
Properties of the catalyst used in this study

Unit cell size (Å)	24.28
BET surface area (m^2/g)	155
Crystal size (μm)	0.9
Na_2O (wt.%)	Negligible

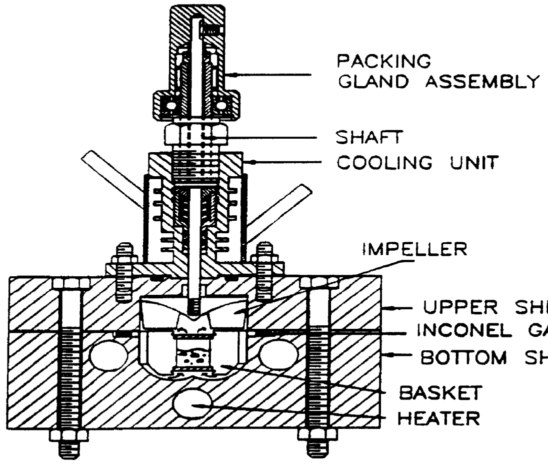
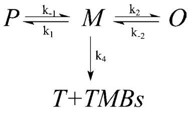


Fig. 1. Schematic diagram of the Riser Simulator.

3. Kinetic modeling

The reaction scheme of xylene isomerization over acid catalysts has been as issue of controversy over the years. The two schemes proposed for the reaction are the sequence and triangular reaction schemes [14]. Both schemes have been used by different researchers for the modeling of xylene isomerization [5,6,7–10,14,27]. The findings of the present study support the sequence reaction scheme for *meta*-xylene transformation over USY zeolite within the limited range of conversion obtained.



In the present work, an attempt is made to develop a suitable kinetic model for the reaction under the present conditions. The model based on the reaction scheme shown above was found to surpass the others as it fitted the obtained experimental data more with a reasonable 95% confidence level for the adjustable model parameters.

The proposed model assumes a sequence reaction network in which there is no direct interconversion between *para*- and *ortho*-xylene. Furthermore, the disproportionation reaction producing toluene and trimethylbenzenes was assumed to be mainly from the *meta*-xylene feed considering that the yield of both *para*- and *ortho*-xylene has a maximum value of 4%. These assumptions are reasonable given that the ratio of the concentration of *meta*- to *para*-xylene and *ortho*-xylene in the reactor is always very high (≈90/4). Besides, employing short reaction time may decrease the rate of the undesired secondary reactions such as the disproportionation of *para*- and *ortho*-xylene into toluene and trimethylbenzenes. A further assumption is that the reactor operates under isothermal condition [15] which is justified by the negligible temperature change during the reaction.

The differential equations describing the kinetics of *meta*-xylene isomerization assuming a first-order isomerization [6,11,14] and disproportionation [14,22] based on the above reaction scheme can be derived from mass balance as follows:

$$\frac{\mathrm{d}y_m}{\mathrm{d}t} = -\left[(k_1 + k_2 + k_4)y_m - \frac{k_1}{K_{pm}}y_p - \frac{k_2}{K_{om}}y_o\right] \times \frac{W_\mathrm{c}}{V}\exp(-\lambda(1 - y_m)) \quad (1)$$

$$\frac{\mathrm{d}y_p}{\mathrm{d}t} = \left[k_1 y_m - \frac{k_1}{K_{pm}}y_p\right]\frac{W_\mathrm{c}}{V}\exp(-\lambda(1 - y_m)) \quad (2)$$

$$\frac{\mathrm{d}y_o}{\mathrm{d}t} = \left[k_2 y_m - \frac{k_2}{K_{om}}y_o\right]\frac{W_\mathrm{c}}{V}\exp(-\lambda(1 - y_m)) \quad (3)$$

$$\frac{\mathrm{d}y_d}{\mathrm{d}t} = k_4 y_m \frac{W_\mathrm{c}}{V}\exp(-\lambda(1 - y_m)) \quad (4)$$

With y_m, y_p, y_o and y_d representing the mass fraction of *meta*-xylene, *para*-xylene, *ortho*-xylene, and disproportionation products, respectively, which are related to the concentration of any species i with the following expression: $C_i = y_i W_\mathrm{hc}/\mathrm{MW}_i V$. $\varphi = \exp(-\lambda(1 - y_m))$ represents catalyst deactivation based on reactant converted (RC) model proposed by Al-Khattaf and de Lasa [16].This type of model has been reported to incorporate a sound mechanistic description of catalyst deactivation [18], and also allows for changes of chemical species without extra requirement of measuring the coke concentration [16]:

$$k_i = k_0 \exp\left(\frac{-E_i}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]\right) \quad (5)$$

where T_0 is the average reaction temperature introduced for re-parameterization of kinetic constants [25,26]:

$$k_{-1} = \frac{k_1}{K_{pm}} \quad (6)$$

$$k_{-2} = \frac{k_2}{K_{om}} \quad (7)$$

where $K_{pm} = (C_p/C_m)_\mathrm{eq}$ and $K_{mo} = (C_o/C_m)_\mathrm{eq}$ are temperature-dependent equilibrium constants for *m*- to *p*-xylene and *m*- to *o*-xylene reactions, respectively, introduced for thermodynamic consistency at equilibrium [7].

4. Results and discussion

4.1. Experimental results

The product distributions for *meta*-xylene isomerization over USY zeolite catalyst under the conditions of the present study were mainly *para*-xylene, *ortho*-xylene, toluene and trimethylbenzenes. Traces of benzene and tetramethylbenzenes were also observed, however, the yields of these products were consistently very low and as a result were neglected in subsequent analysis.

It is important to notice that the *P*/*O* ratios observed in the present study were below the equilibrium ratio of 1.09 [28] for all the experimental runs in accordance with some published works [29,30,31,32]. The reason for the lower values below the equilibrium ratio can be explained due to the significance of bimolecular isomerization reaction between the *meta*-xylene and trimethylbenzene producing more of *ortho*-xylene compared to *para*-xylene [32]. This is expected since USY has enough internal porosity to accommodate the bulky bimolecular isomerization transition state resulting from its large internal cages. To verify this point, we employed the method proposed by Morin et al. [32], by plotting *P*/*O* selectivity against D/I ratios at ∼10 and 14% conversion levels, respectively, as shown in Fig. 2. From this figure, it can be observed that the greater the D/I the lower the *P*/*O*, this could indicate that the bimolecular isomerization process whose significance increases with D/I is more selective to *ortho*-xylene than the monomolecular process [32].

In order to understand the behaviour of *meta*-xylene transformation reaction over the catalyst, we attempted to study the effect of conversion and temperature on the D/I and *P*/*O* ratios. As shown in Fig. 3A, the D/I ratio was found to increase steadily with increase in the level of *meta*-xylene conversion. This is not surprising, since the selectivity to trimethylbenzenes increases with conversion, and the bimolecular isomerization reaction involves trimethylbenzenes intermediates [33]. On the other hand, the *P*/*O* ratio

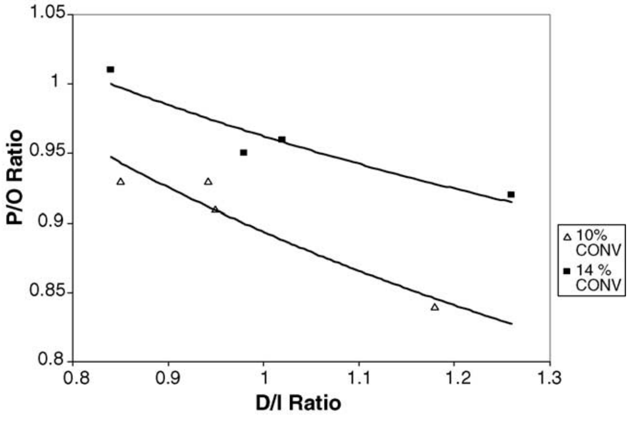


Fig. 2. *Para*/*ortho*-xylene (*P*/*O*) ratio vs. disproportionation/isomerization ratio (D/I) at 10 and 14% of *m*-xylene conversion.

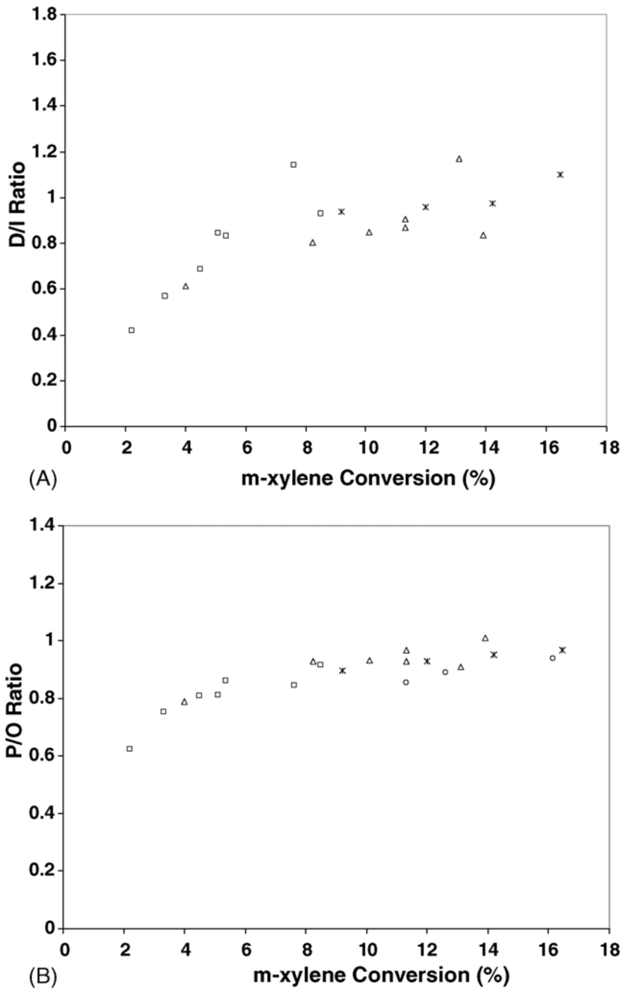


Fig. 3. (A) Disproportionation/isomerization (D/I) ratio versus *m*-xylene conversion; (B) *p*-xylene/*o*-xylene (*P*/*O*) ratio vs. *m*-xylene conversion.

increases with conversion until it reaches a maximum value close to 1 (Fig. 3B). This slight increase might be due to a kinetic effect [29]. Also, the effect of temperature on D/I and *P*/*O* at 10 and 14% conversion is shown in Fig. 4, respectively. It can be seen that while D/I increased from 0.8 at 450 °C to around 1.3 at 550 °C for both conversions, *P*/*O* decreased from 1 to 0.93 (Fig. 4A and B). Thus, it is very clear that D/I ratio is more sensitive to temperature than *P*/*O* ratio. The increase of D/I ratio with temperature is likely due to the higher activation energy of disproportionation reaction as compared with isomerization reaction, while the mild effect of temperature on *P*/*O* may be explained in terms of the similarity of activation energies of both compounds (see Table 2).

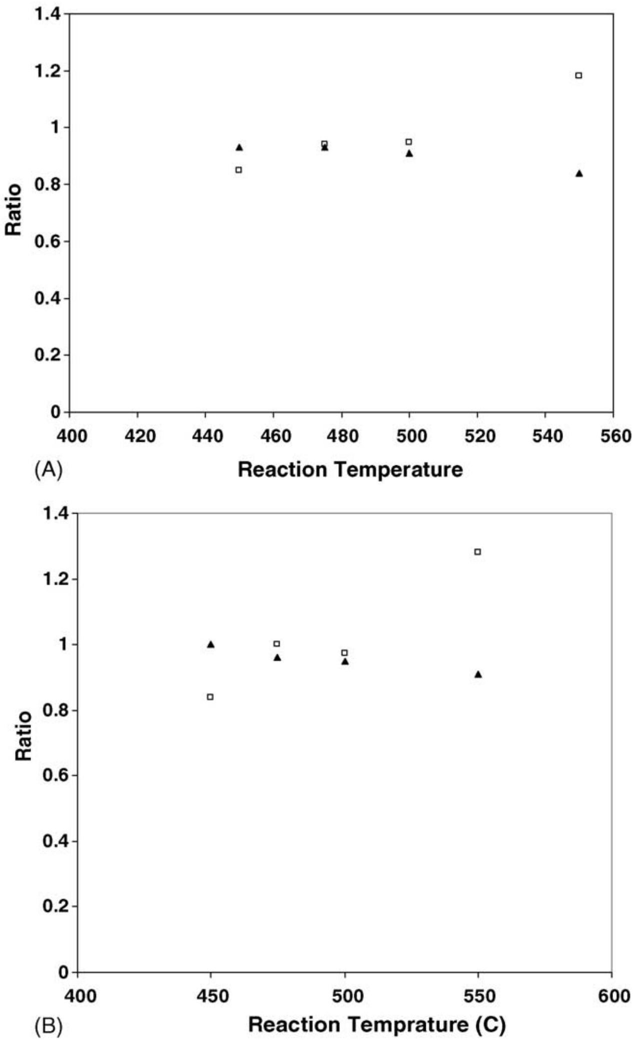


Fig. 4. (A) *P*/*O* and D/I ratios vs. reaction temperature at 10% conversion: (☐) D/I ratio and (▲) *P*/*O* ratio. (B) *P*/*O* and D/I ratios vs. reaction temperature at 14% conversion: (☐) D/I ratio and (▲) *P*/*O* ratio.

The approach to equilibrium (ATE) can be defined as

$$\frac{F - P_i}{F - E_i} \times 100 \tag{8}$$

where F is the feed concentration of *m*-xylene, P_i the product concentration of *p*- or *o*-xylene and E_i the equilibrium concentration of *p*- or *o*-xylene. This is a useful parameter in evaluating the relative reaction rate of both isomerization reaction pathway [6]. As observed from the plot of ATE of *m*-xylene as a function of conversion (Fig. 5), *p*- and *o*-xylene approaches their equilibrium value at almost the same rate. However, the ATE for *o*-xylene is about 20% more than that

Table 2
Estimated kinetics parameters

	k_{01} ($\times 10^3$)	E_1	k_{02} ($\times 10^3$)	E_2	k_{04} ($\times 10^3$)	E_4	λ	r^2
	0.19	17	0.22	15.5	0.54	18.8	0.9	0.99
95% CFL	0.02	2.1	0.02	1.8	0.06	1.4	0.1	

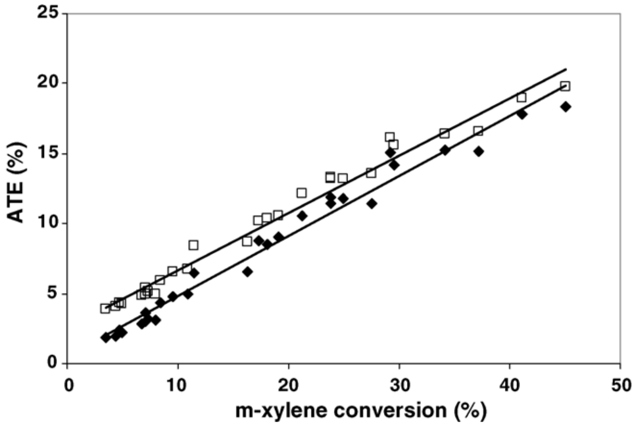


Fig. 5. Approach to equilibrium for *p*- and *o*-xylene vs. *meta*-xylene conversion: (⧫) *p*-xylene and (□) *o*-xylene.

of *p*-xylene indicating that *o*-xylene should have a slightly higher reaction rate during *m*-xylene transformation. This is in line with the obtained kinetic parameters as will be discussed in the next section.

4.2. Determination of kinetic parameters

A computer program in a MATLAB package was developed using the classical fourth-order Runge–Kutta method of fixed interval size in order to determine the model parameters in Eqs. (1)–(7). The values of the kinetic constants and activation energies obtained with their corresponding 95% confidence limits (nonlinear hypothesis) are presented in Table 2.

It can be observed from Table 2 that E_4 is the largest which indicates that the activation energy required to move out a methyl group as a result of xylene disproportionation is higher than that for intramolecular methyl transfer in xylene isomerization by magnitudes of 3–4 kcal/mol. Furthermore, it was also noted that the activation energies for the isomerization of *meta*-xylene to *ortho*-xylene, E_1 and *meta*-xylene, E_2 are closely. This can be easily understood; the isomerization of *m*-xylene to produce *p*- and *o*-xylene involves 1, 2 methyl shifts along the benzene ring which are identical reactions. Moreover, the cage opening of USY zeolite is large enough and thus allows the produced isomers to exit the zeolite cage openings presumably without any shape selectivity. This observation is in good agreement with previous studies [3,8,14].

4.3. Model prediction

Figs. 6–9 show the comparison between the model predictions and the experimental data at various temperatures. As observed in these plots, the model predictions compare favourably with the obtained experimental data for the various conditions, indicating that the model can be used to accurately represent the experimental data following the assumptions made, coupled with the peculiar nature of this process in the Riser Simulator. In addition, the reconcilia-

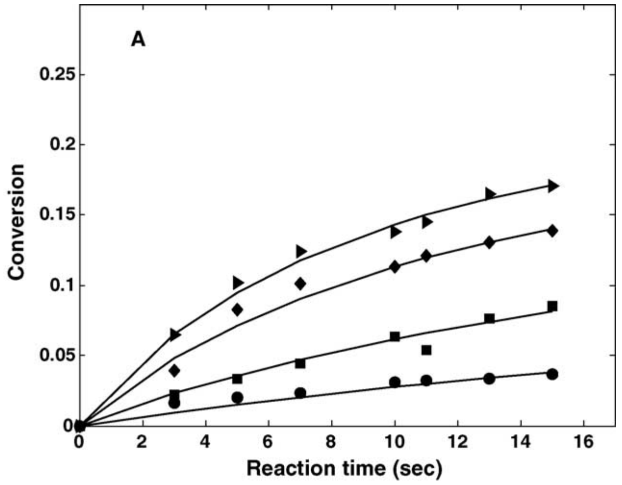


Fig. 6. Comparison between experimental results and model predictions for *meta*-xylene conversion: (●) 350 °C, (■) 400 °C, (⧫) 450 °C and (▶) 475 °C.

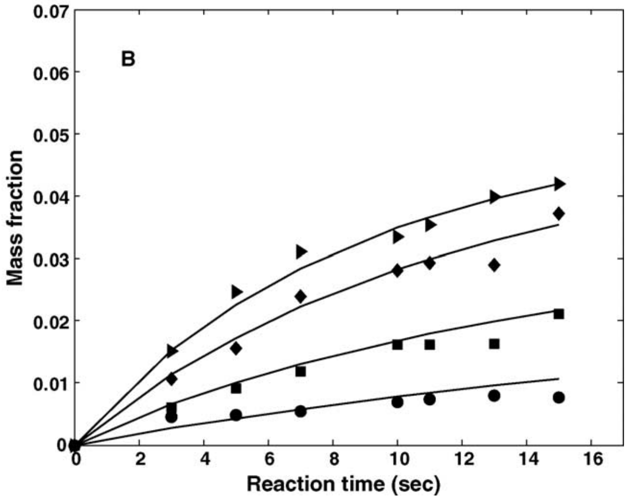


Fig. 7. Comparison between experimental results and model predictions for *para*-xylene yield: (●) 350 °C, (■) 400 °C, (⧫) 450 °C and (▶) 475 °C.

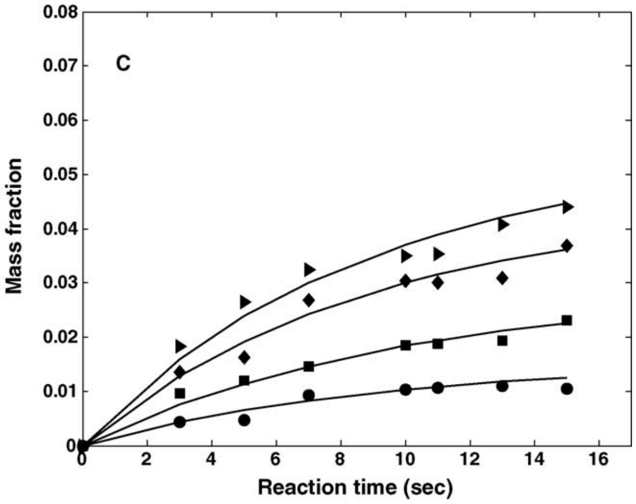


Fig. 8. Comparison between experimental results and model predictions for *ortho*-xylene yield: (●) 350 °C, (■) 400 °C, (⧫) 450 °C and (▶) 475 °C.

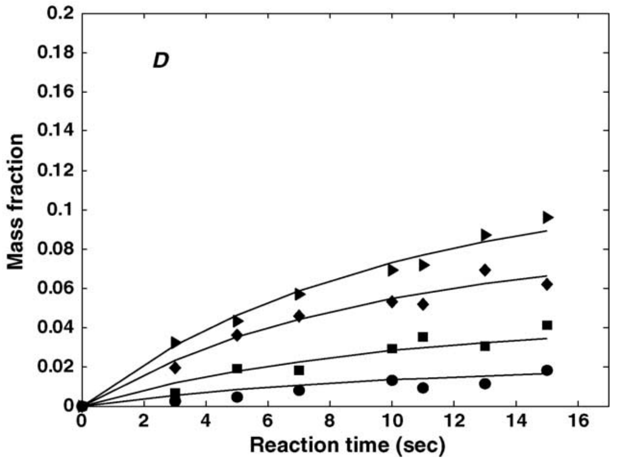


Fig. 9. Comparison between experimental results and model predictions for T + TMBs yield: (●) 350 °C, (■) 400 °C, (⧫) 450 °C and (▶) 475 °C.

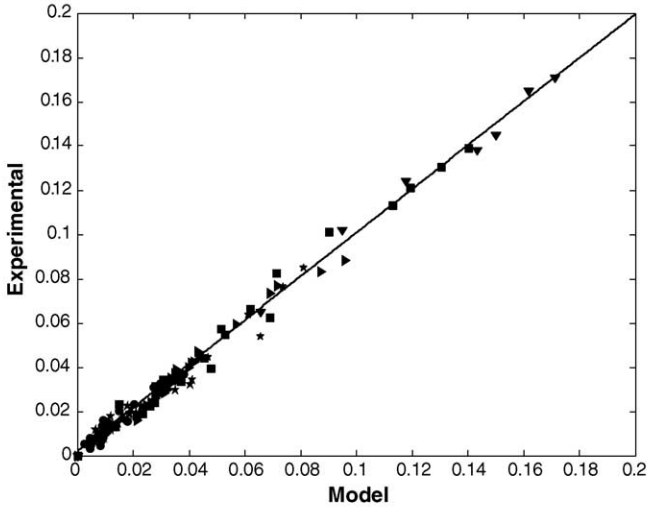


Fig. 10. Overall comparison between the experimental results and model predictions: (●) 350 °C, (■) 400 °C, (⧫) 450 °C and (▶) 475 °C.

tion plots (Fig. 10) between the experimental data and the model predictions display a normal distribution of residuals, besides, the adequacy of the model and the selected parameters to fit the data as shown in Table 2 gave 0.999 regression coefficients.

5. Conclusion

1. The kinetics of gas-phase isomerization of *meta*-xylene has been successfully investigated over USY zeolite in a Riser Simulator.
2. The significance of the bimolecular isomerization which is selective to *ortho*-xylene is apparent, and it becomes more prominent with increasing level of *meta*-xylene conversion.
3. The D/I ratio increases steadily with both *m*-xylene conversion and reaction temperature whereas *P*/*O* ratio is only mildly affected with both reaction parameters.
4. The apparent activation energies for the isomerization of *meta*-xylene to *ortho*- and *para*-xylene is closely similar, while that of disproportionation is higher.
5. The close comparison between the model predictions and the obtained experimental data indicate that the Riser Simulator can be used as an effective tool in the investigation of the kinetics of *meta*-xylene isomerization.

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