

1,2,4-Trimethylbenzene Transformation Reaction Compared with its Transalkylation Reaction with Toluene over USY Zeolite Catalyst

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1,2,4-Trimethylbenzene (TMB) transalkylation with toluene has been studied over USY zeolite type catalyst using a riser simulator that mimics the operation of a fluidized-bed reactor. Reaction mixtures of 50:50 wt % TMB and toluene were used for the transalkylation reaction. The range of temperature investigated was 400–500 °C with time on stream ranging from 3 to 15 s. The effect of reaction conditions on the variation of the *p*-xylene to *o*-xylene product ratio (P/O), distribution of trimethylbenzene (TMB) isomers (1,3,5-TMB to 1,2,3-TMB), and values of xylene/tetramethylbenzene (X/TeMB) ratios are reported. Comparisons are made between the results of the transalkylation reaction with the results of pure 1,2,4-TMB and toluene reactions earlier reported. Toluene, which was found almost inactive, became reactive upon blending with 1,2,4-TMB. This shows that toluene would rather accept a methyl group to transform to xylene than lose a methyl group to form benzene under the present experimental conditions. The experimental results were modeled using a quasi-steady-state approximation. Kinetic parameters for the 1,2,4-TMB disappearance during the transalkylation reaction and in its conversion into isomerization and disproportionation products were calculated using the catalyst activity decay function based on time on stream (TOS). The apparent activation energies were found to decrease as follows: $E_{\text{transalkylation}} > E_{\text{isomerization}} > E_{\text{disproportionation}}$.

1. Introduction

The demand for xylenes as a raw material for polyester fibers and films continues to grow and drive the search to increase xylene production processes. In 1999, the world consumption of mixed xylene was about 24 million tons, and it is expected to grow at a rate of 6.2% to 35.9 million tons by 2007. This indicates that xylenes are still gaining importance in the petrochemical market. Among the three xylene isomers, *p*-xylene is the most demanded and thus most expensive, followed by *o*-xylene.

One common way for xylene production is the conversion of the lower value toluene (C₇) and trimethylbenzene (C₉) into xylenes via toluene disproportionation, trimethylbenzene (TMB) disproportionation, and transalkylation with toluene. Thus, these processes offer a way to utilize the low-cost toluene and TMB to produce the much more attractive product xylene. The major commercial transalkylation processes are the Xylene-Plus process developed by ARCO-IFP, the Tatoray process developed by UOP, and the TransPlus process developed by Mobil-CPC.^{1,2}

Zeolites such as Y, zeolite beta, and modernite possess a pore size large enough for transformation of TMB. Cejka et al.³ studied the effect of the structure of large-pore zeolites of beta, Y, L, and mordenite on TMB disproportionation. Wang et al.¹ used zeolite beta to investigate its potential in xylene production reactions, including toluene disproportionation, TMB disproportionation, and toluene–TMB transalkylation. They found that zeolite beta has excellent stability and transalkylation selectivity. In TMB disproportionation, blending toluene into feedstocks can shift the production selectivity of tetramethylbenzene (TeMB) to xylene, whereas in toluene disproportionation, mixing TMB into feedstocks not only reduced the reaction temperatures but also raised the xylene yield. Das et al.⁴ also

studied the toluene and TMB transformation reactions using zeolite beta. They obtained the highest yield of xylenes at a temperature of 400 °C and toluene/TMB molar ratio of about 1:1.

Over medium-pore zeolites, TMB transformations revealed a much lower yield of xylenes compared to that under large-pore and high acidity zeolites.^{5–8} Roger et al.⁷ studied the conversion of 1,2,4-TMB over HZSM5. They observed that isomerization of 1,2,4-TMB to 1,2,3- and 1,3,5-TMB isomers was found to be the most rapid reaction with about 90% selectivity at low conversion and the 1,2-methyl shift was shown to take place on the external surface of the zeolite crystals. They noted that the disproportionation of 1,2,4-TMB was followed by rapid paring dealkylation of the TeMBs. The bulky intermediates (TeMBs) that reinforced the diffusional resistances by pore mouth narrowing favored the paring reaction inside the zeolite crystals.

The above literature survey indicates that most of the research on the TMB transformations has been carried out in fixed-bed reactors.^{1–8} Fluidized bed on the other hand reveals the importance of diffusional effects in these reactions. Atias et al.⁹ investigated the conversion of 1,2,4-TMB in a riser simulator fluidized bed using USY zeolite catalysts under relevant FCC conditions. Their results showed that 1,2,4-TMB underwent both isomerization and disproportionation. The authors also modeled the kinetic reactions using both time-on-stream and reactant-converted (RC) models.

Al-Khattaf et al.¹⁰ studied the transformation of toluene, xylenes, and TMB over Y-zeolite catalyst in a riser simulator. They found that the sequence of reactivity of the three alkyl benzenes decreases as the number of methyl group per benzene ring decreases, as follows: 1,2,4-trimethylbenzene > *m*-xylene > toluene. Toluene was found unreactive in the temperature range studied of 350–500 °C. They concluded that the number of methyl groups has the most important role in the reactivity of 1,2,4-TMB, *m*-xylene, and toluene over Y-based catalyst.

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However, toluene was found to be reactive only when Y zeolite with higher acidity was used.¹¹

Dumitriu et al.¹² studied the transalkylation of toluene with TMB catalyzed by various AFI catalysts. They investigated the effect of the isomorphous substitution of various metals in the AIPO-5 framework on the catalytic transalkylation of toluene with trimethylbenzene. They concluded that, generally, the transalkylation and/or disproportionation reactions occur on stronger acid sites, while the isomerization of xylenes (X's) and TMBs predominate on weaker acid sites. Cejka and Wichterlova¹³ indicated that the concentration of active sites and zeolite structure have the most significant impact on the activity and selectivity in TMB transalkylation with toluene. They also reported that the addition of toluene to TMB significantly reduces the rate of TMB dealkylation. Furthermore, a toluene/TMB molar ratio of 1 in the feed was provided as the optimum for xylene production, similar to other another reported study.⁴

The present study is aimed at investigating the transalkylation of TMB with toluene to produce xylenes over Y zeolite type catalyst (FCC-Y) in a fluidized-bed reactor. The study will focus on the effect of reaction conditions (time, temperature, and conversion) on xylene yields, *p*-xylene to *o*-xylene (P/O) ratio, and 1,3,5- to 1,2,3-TMB ratio. Comparisons will also be made with our earlier reported studies on catalytic transformations of toluene and 1,2,4-TMB, each alone.^{10,11} An attempt will also be made to model the transalkylation reaction of 1,2,4-TMB with toluene, taking into consideration the major side reactions taking place.

2. Experimental Procedures

2.1. The Riser Simulator. All the experimental runs were carried out in a riser simulator. This reactor is novel bench-scale equipment with an internal recycle unit invented by de Lasa.¹⁴ The riser simulator consists of two outer shells, the lower section and the upper section, which allow easy loading or unloading of the catalyst. 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 is forced outward from the center of the impeller toward the walls. This creates a lower pressure in the center region of the impeller, thus inducing 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.¹⁵

2.2. Materials. 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. The process of sodium removal was repeated for the pelletized 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, forming FCC-Y catalyst used in our studies.

Analytical grade (99% purity) toluene and 1,2,4-trimethylbenzene were obtained from Sigma-Aldrich. All chemicals were used as received, as no attempt was made to further purify the samples.

2.3. 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); 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; in the same manner the timer was adjusted to the desired reaction time. At this point the gas chromatograph (GC) was started and set to the desired conditions.

Once the reactor and the gas chromatograph 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 opened, ensuring that the reaction was terminated and the entire product stream sent on-line to the analytical equipment via a preheated 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.

The reactant injection was carried out at atmospheric pressure. Subsequently, the pressure increased upon reactant vaporization. The reaction pressure of the system after reactant vaporization was about 2.0–2.5 atm. However, the reaction period developed at essentially constant pressure. This is equivalent to having total constant pressure since the total number of moles remains constant.

Coke deposited on 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

Catalytic experiments were carried out in the riser simulator at a catalyst/reactant ratio of 5 (weight of catalyst = 0.81 g, weight of reactant injected = 0.162 g); residence times of 3, 5, 7, 10, 13, and 15 s; and temperatures of 400, 450, and 500 °C. During the course of the investigation, a number of runs were repeated to check for reproducibility in the conversion results, which was found to be excellent. Typical errors were in the range of $\pm 2\%$.

3.1. Catalyst Characterization. The BET surface area was measured according to the standard procedure ASTM D-3663, using a NOVA 1200 unit (QUANTA CHROME). 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 outgassed at 400 °C for 30 min in flowing He and then cooled to 150 °C. At that temperature, NH_3 was adsorbed on the sample by injecting pulses of 2 μL /pulse. The

Table 1. Characterization of Used USY Zeolite Catalysts

catalyst	acidity (mmol/g)	BET surf. area (m ² /g)	crystallite size (nm)	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

Table 2. Product Distribution (wt %) at Various Reaction Conditions for the 1,2,4-Trimethylbenzene Transformation Reactions

temp (°C)/time (s)	conv (%)	Product Distribution (wt %)										elem C bal (%)	
		gas	benzene	1,3,5-TMB	1,2,3-TMB	TI ^a	<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene	toluene	TeMBs ^b		TD ^c
400													
5	12.6			2.0	1.0	3.0	0.9	2.1	1.3	0.5	3.7	8.0	99.6
10	23.0	0.1		3.8	1.8	5.6	1.7	4.0	2.5	0.8	8.0	16.2	99.5
15	31.3	0.1	0.0	5.2	2.5	7.7	2.3	5.5	3.4	1.2	11.6	22.7	99.4
450													
5	15.6	0.1		2.6	1.3	3.9	1.1	2.5	1.5	0.6	4.8	9.8	99.6
10	26.9	0.1		4.4	2.1	6.6	1.9	4.3	2.6	1.0	9.0	17.8	99.5
15	36.0	0.2	0.1	6.0	2.8	8.8	2.5	5.8	3.4	1.4	12.2	23.8	99.3
500													
5	16.2	0.2		2.7	1.3	4.1	1.1	2.6	1.5	0.7	4.9	10.1	99.6
10	28.2	0.3	0.1	4.7	2.3	7.0	2.0	4.5	2.6	1.2	9.1	18.1	99.3
15	38.0	0.5	0.1	6.2	2.9	9.1	2.7	6.3	3.5	1.7	11.8	24.3	99

^a TI, total isomerization. ^b 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-TeMBs. ^c TD, total disproportionation.

Table 3. Product Distribution (wt %) at Various Reaction Conditions for 50 wt % 1,2,4-Trimethylbenzene Transalkylation with 50 wt % Toluene

temp (°C)/time (s)	conversion (%)										elem C bal (%)	
	T	TMB	gas	benzene	1,3,5-TMB	1,2,3-TMB	<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene	xylenes		TeMBs ^a
400												
5	2.44	14.02		0.19	1.17	0.50	1.47	2.41	1.55	5.43	0.92	98
7	3.80	18.88		0.24	1.48	0.69	2.04	3.35	2.18	7.57	1.33	98
10	5.34	24.80		0.28	1.90	0.94	2.68	4.37	2.91	9.96	1.99	97.9
13	5.96	29.68		0.32	2.26	1.13	3.15	5.14	3.43	11.72	2.43	97.8
15	7.10	31.76		0.37	2.42	1.17	3.48	5.69	3.79	12.96	2.71	97.8
450												
5	3.50	16.30		0.30	1.84	0.79	2.12	4.15	2.21	8.48	1.10	97
7	6.04	22.84		0.37	2.01	0.91	2.49	4.45	2.61	9.55	1.50	97.8
10	8.10	29.16		0.48	2.38	1.16	3.26	5.75	3.43	12.44	2.09	97.9
13	10.00	34.50		0.59	2.99	1.40	3.96	7.24	4.09	15.29	2.43	98
15	11.34	36.68	0.06	0.56	3.23	1.55	4.13	7.44	4.32	15.89	2.65	98
500												
5	4.46	17.14		0.31	1.56	0.66	1.87	3.43	1.93	7.23	1.02	98
7	8.04	24.94	0.06	0.57	2.32	1.01	2.74	5.41	2.84	10.99	1.43	98
10	10.52	30.64	0.08	0.76	2.69	1.21	3.46	6.86	3.61	13.93	1.81	97.9
13	13.42	36.74	0.11	0.84	3.30	1.54	4.21	8.32	4.40	16.93	2.24	98
15	15.20	39.74	0.11	0.96	3.52	1.65	4.62	9.13	4.81	18.56	2.50	97.9

^a 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-TeMBs.

Table 4. Coke Formation for 1,2,4-TMB Transformation Reaction and Its Transalkylation Reaction with Toluene at Different Reaction Conditions

temp (°C)/time (s)	1,2,4-TMB alone			1,2,4-TMB + toluene (50:50)		
	conv (%)	coke (wt %)	coke/conv	conversion [1,2,4-TMB] (%)	coke (wt %)	coke/conv
400						
5	12.6	0.30	0.02	14.02	0.23	0.02
10	23.0	0.36	0.02	24.80	0.36	0.01
15	31.3	0.37	0.01	31.76	0.44	0.01
500						
5	16.2	0.18	0.01	17.4	0.14	0.01
10	28.2	0.20	0.01	30.64	0.21	0.01
15	38.0	0.23	0.01	39.74	0.29	0.01

injection was repeated until the amount of NH₃ detected was the same for the last two injections. After the adsorption of NH₃ was saturated, the sample was flushed at 150 °C for 1 h with He to remove excess NH₃, 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 NH₃. The results of the catalyst characterization are summarized in Table 1.

3.2. Toluene Disproportionation and 1,2,4-Trimethylbenzene Reactions (Each Alone). Disproportionation reaction of toluene alone over FCC-Y catalyst was reported in our earlier

publication.¹⁰ No transformation of toluene into xylenes was observed for this catalyst. The result was attributed to the low acidity of the Y zeolite (0.033mmol/g), possibly much lower than the minimum value required to transform toluene into xylenes. Moreover, toluene disproportionation seems to require high pressure to take place while these runs were conducted in the riser simulator at relatively low pressure (2–2.5 atm).

The results of transformation reaction of 1,2,4-TMB over FCC-Y alone at different reaction temperatures and contact times have also been reported by Al-Khattaf et al.¹⁰ The product distribution is partially reproduced in Table 2. The experimental

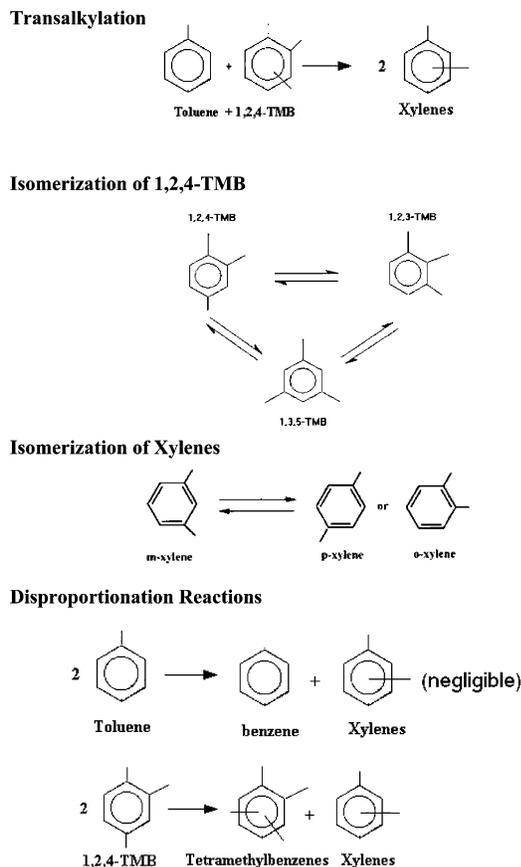


Figure 1. Reactions occurring during transalkylation reaction of 1,2,4-trimethylbenzene with toluene.

results showed that conversion of up to 38% was observed at 15 s and reaction temperature of 500 °C.

3.3. Transalkylation of 1,2,4-TMB with Toluene. The results of transalkylation of 1,2,4-TMB with toluene (50:50 wt %) at different reaction temperatures and contact times are presented in Table 3. Previous studies^{1,2} have shown that the 50:50 wt % reactant ratio generally produces higher xylene yields. The experimental results showed that the desired reaction, i.e., transalkylation of 1,2,4-TMB and toluene to xylenes, is accompanied by disproportionation and isomerization of trimethylbenzenes (1,2,4, 1,2,3, and 1,3,5 isomers), as well as xylene isomerization (ortho, meta, and para isomers). In addition, the disproportionation of toluene was found negligible. Dealkylation reaction is inconsequential due to the minor amounts of gases in the reaction system. This parallel-consecutive reaction system is therefore characterized by multiple chemical equilibria.¹⁶ The various individual reactions identified during transalkylation of 1,2,4-TMB with toluene are given in Figure 1.

The data from the transalkylation reaction show that higher amounts of 1,3,5-TMB were found compared to 1,2,3-TMB. Furthermore, three different isomers of tetramethylbenzenes (TeMBs) were detected (1,2,4,5-TeMB, 1,2,3,5-TeMB, and 1,2,3,4-TeMB). Pentamethylbenzene (PeMB) has been found to be negligible. The experiment results also suggest that the ratio of *p*-xylene to *o*-xylene follows closely the thermodynamic equilibrium value of 1.0¹⁷ irrespective of mixture compositions.

Table 3 also shows that 1,2,4-TMB and toluene conversions increase with temperature as well as with reaction time. At 15 s, toluene conversion rose from 7.1% at 400 °C to about 15.2% at 500 °C. At the same reaction time of 15 s, the conversion of 1,2,4-TMB also increased from 31.76% at 400 °C to 39.74% at 500 °C.

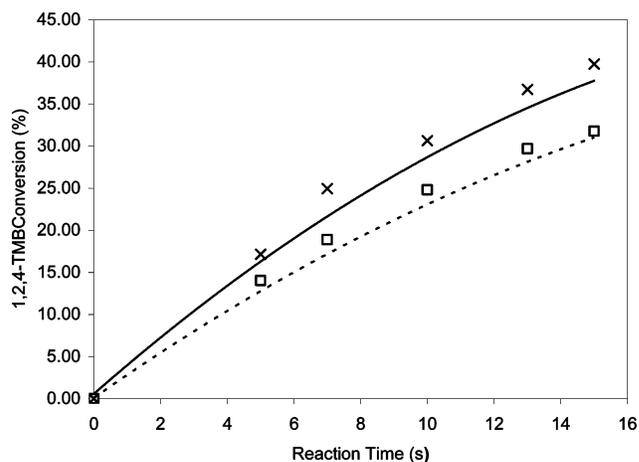


Figure 2. Reactivity comparisons between 1,2,4-TMB reaction alone at (---) 400 and (—) 500 °C, and transalkylation reaction of 1,2,4-TMB with toluene at (□) 400 and (×) 500 °C.

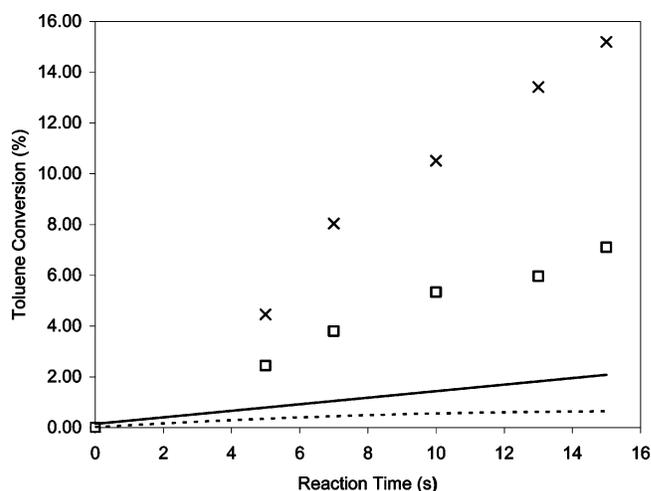


Figure 3. Reactivity comparisons between toluene reaction alone at (---) 400 and (—) 500 °C, and transalkylation reaction of 1,2,4-TMB with toluene at (□) 400 and (×) 500 °C.

Coke was also measured at different conditions. Table 4 reveals the amount of coke deposition. It is clear that the ratio of coke weight percent to percent conversion is very small, ranging from 0.01 to 0.02 at all reaction conditions for both 1,2,4-TMB alone and for 50:50 wt % 1,2,4-TMB-toluene mixture.

3.4. Transalkylation of 1,2,4-TMB with Toluene vs Results of Reactions of 1,2,4-TMB and Toluene, Each Alone. **3.4.1. Reactivity.** Conversions of 1,2,4-TMB are plotted versus reaction time in Figure 2 at 400 and 500 °C, respectively. The plots show that 1,2,4-TMB is slightly more reactive during transalkylation reaction with toluene. Similarly, conversions of toluene have been plotted over FCC-Y catalyst in Figure 3. Toluene conversion of up to 15.2% was observed at 15 s and reaction temperature of 500 °C during the transalkylation reaction.

Toluene was found almost inactive alone under our reaction conditions as reported in ref 10. Since a very negligible amount of toluene was found during the transformation reaction of 1,2,4-TMB alone as presented in Table 2 and ref 10, the reactivity of toluene can only be attributed to the transalkylation reaction. By blending trimethylbenzene with toluene, the average methyl group number per benzene ring is increased, leading to higher reactivity as pointed out in ref 1. This shows that toluene would rather accept a methyl group to transform to xylene than lose a

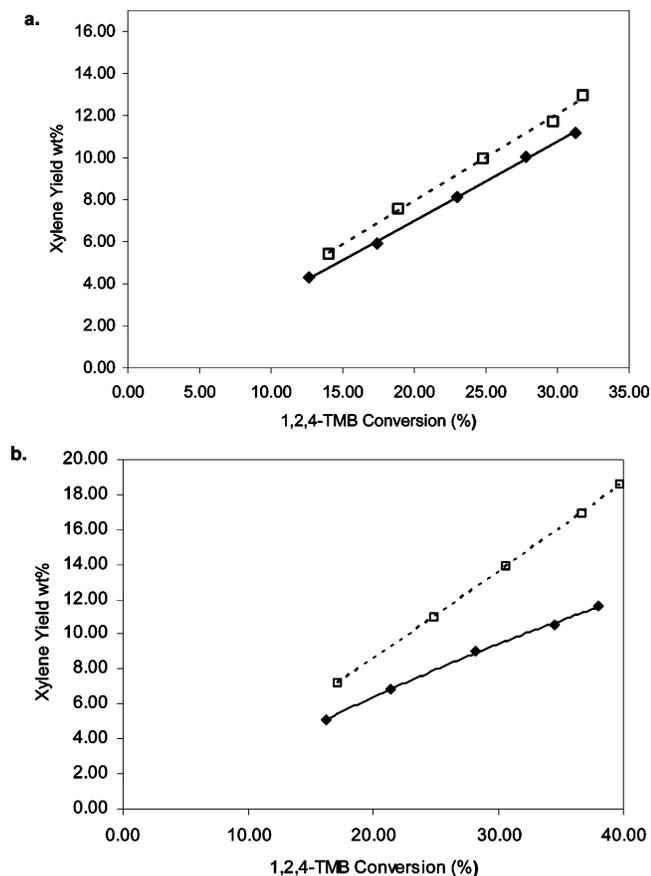


Figure 4. Xylene yield comparisons between 1,2,4-TMB reaction alone (◆) and transalkylation reaction of 1,2,4-TMB with toluene (□) at (a) 400 and (b) 500 °C.

methyl group to form benzene under the present experimental conditions with pressures around 2–2.5 atm.

3.4.2. Xylene Yield. Xylene yields in weight percent were plotted versus 1,2,4-TMB conversion for both transalkylation reaction and trimethylbenzene reaction alone in Figure 4 over the FCC-Y catalyst. From the plots, it is observed that the amount of xylenes formed during the transalkylation reaction was higher than with pure 1,2,4-TMB reaction at all temperatures studied. The highest xylene yield was found to be approximately 18.56 wt % at 39.74% conversion of 1,2,4-TMB during the transalkylation reaction, compared to 11.6% for the 1,2,4-TMB reaction alone. The xylene yields are significantly smaller than those reported over zeolite beta,¹ where higher levels of conversions were reported. Tsai et al.¹⁸ reported that adding 4 wt % TMB to commercial toluene disproportionation reaction led to xylene yield increases to 62 vol % from 58 vol %. In general, it can be said that transalkylation boosts xylene production more than disproportionation.

The thermodynamic equilibrium compositions of aromatics during transalkylation reaction are governed by the methyl groups per benzene ring (M/R) of the feedstocks.^{1,2} For disproportionation of pure toluene, the M/R ratio is unity. Mixing 1,2,4-TMB with toluene feed increases the M/R ratio, thereby enhancing xylene yield at the expense of benzene yield.¹ The reactants in this study are in 50:50 ratios, thereby giving an M/R ratio of 2. The maximum thermodynamic equilibrium xylene yield is achieved at an M/R ratio of 2 as reported in ref 2.

3.4.3. *p*-Xylene to *o*-Xylene (P/O) Ratio. The ratios of *p*- to *o*-xylene (P/O) in the product mixture are presented in Figure 5 over the FCC-Y catalyst for the transalkylation reaction as

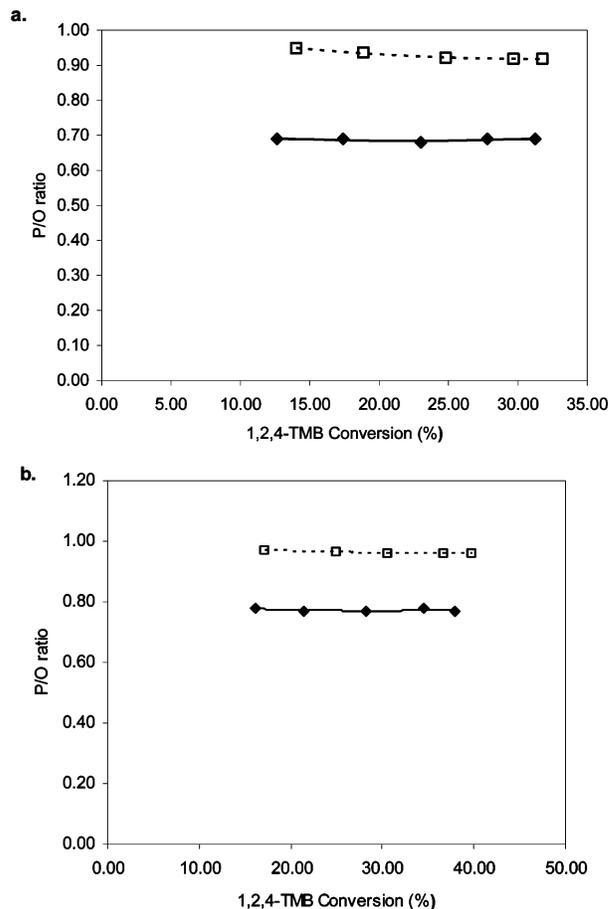


Figure 5. P/O ratio comparisons between 1,2,4-TMB reaction alone (◆) and transalkylation reaction of 1,2,4-TMB with toluene (□) at (a) 400 and (b) 500 °C.

well as for the 1,2,4-TMB reaction alone. The P/O ratio for the transalkylation reaction averages 0.96 over the whole conversion range at both 400 and 500 °C. The P/O ratio is very close to the equilibrium value of 1.0. However, for the pure 1,2,4-TMB reaction, the P/O ratio is between 0.7 and 0.8. The 1,2,4-TMB disproportionation reaction is more selective to *o*-xylene, and this is in agreement with the literature.^{1,2} However, it seems 1,2,4-TMB and toluene transalkylation produces *p*- and *o*-xylenes in equal proportions, consistent with equilibrium compositions. Mirth et al.¹⁹ have indicated that the transition state plays a role in this reaction. Jones et al.²⁰ reported that for large-pore zeolites such as the one under study, where it is highly likely that a bimolecular mechanism operates, P/O ratios below the thermodynamic ratio of ≈ 1 are possible.

3.4.4. 1,3,5-TMB to 1,2,3-TMB Ratio. Zeolites with large cages generally should favor the formation of the larger 1,3,5-TMB molecule, while small-pore zeolites favor 1,2,3-TMB isomer. Experimental results for both the transalkylation reaction and the pure 1,2,4-TMB reaction have shown that higher amounts of 1,3,5-TMB were found compared to 1,2,3-TMB.

Figure 6 depicts the relationship between the 1,3,5-TMB/1,2,3-TMB ratio and conversion. For both reactions, FCC-Y gave a 1,3,5-TMB/1,2,3-TMB ratio of about 2.1 for all experimental conditions. This is not far from the thermodynamic equilibrium value of 2.7 reported over USY at 344 °C.¹⁷

3.4.5. 1,3,5-TMB Yield. Although the ratio of 1,3,5-TMB to 1,2,3-TMB was found to be more or less the same for transalkylation reaction of 1,2,4-TMB and toluene and the reaction of pure 1,2,4-TMB, the amount of either 1,3,5-TMB or 1,2,3-TMB produced is significantly different. Figure 7 shows

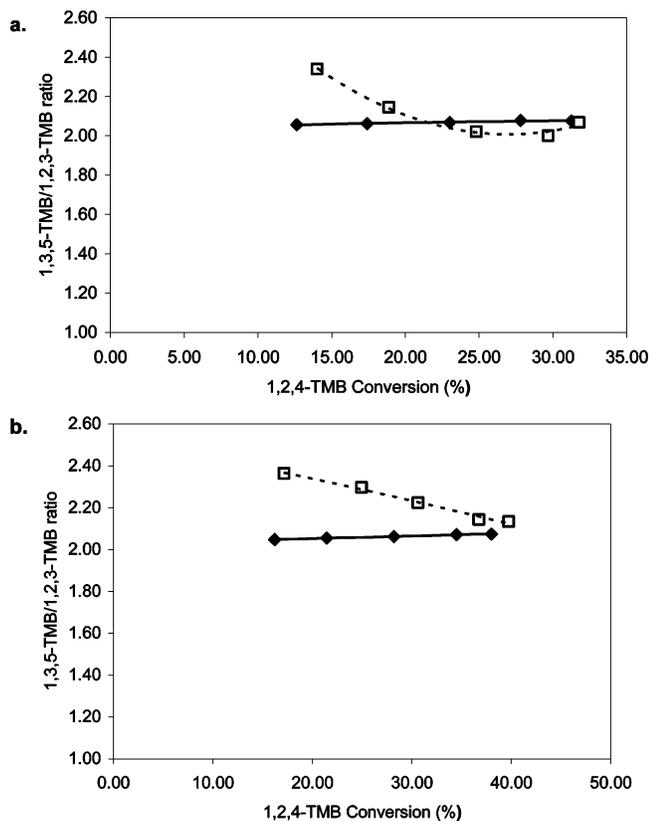


Figure 6. 1,3,5-TMB/1,2,3-TMB ratio comparisons between 1,2,4-TMB reaction alone (◆) and transalkylation reaction of 1,2,4-TMB with toluene (□) at (a) 400 and (b) 500 °C.

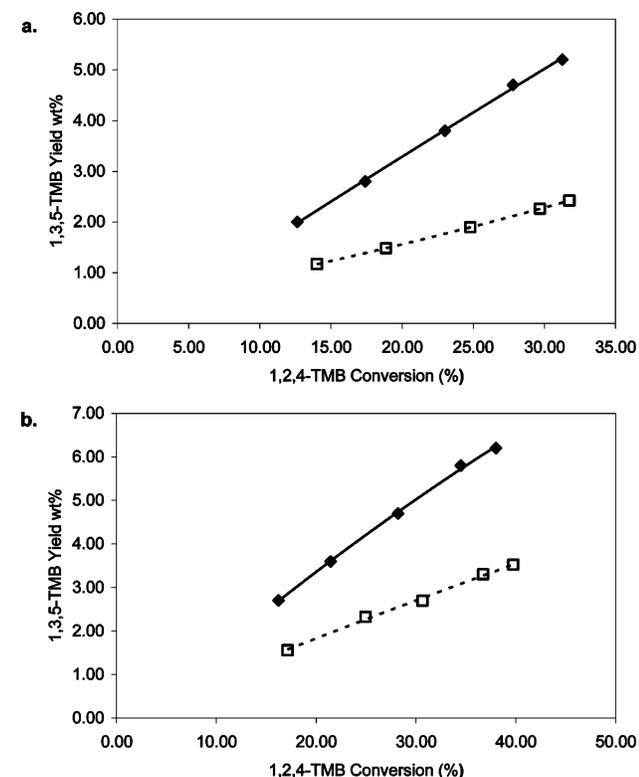


Figure 7. 1,3,5-TMB yield comparisons between 1,2,4-TMB reaction alone (◆) and transalkylation reaction of 1,2,4-TMB with toluene (□) at (a) 400 and (b) 500 °C.

plots of 1,3,5-TMB yields in weight percent versus 1,2,4-TMB conversion for both transalkylation reaction and trimethylbenzene reaction alone over the FCC-Y catalyst. From the plots, it

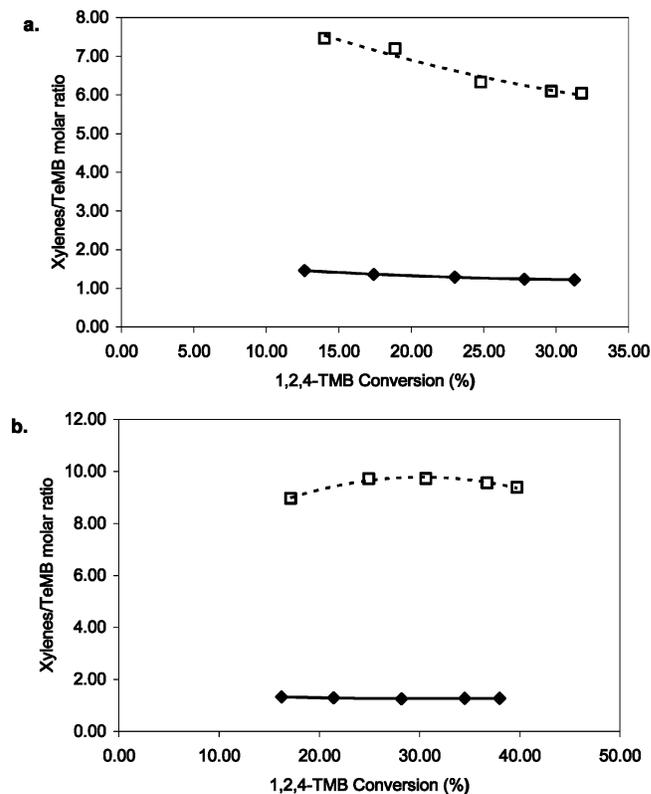


Figure 8. X/TeMB ratio comparisons between 1,2,4-TMB reaction alone (◆) and transalkylation reaction of 1,2,4-TMB with toluene (□) at (a) 400 and (b) 500 °C.

Table 5. Estimated Kinetic Parameters Based on Time on Stream (TOS Model)

parameters	values		
	k_{trans}	k_{iso}	k_{disp}
E_i (kJ/mol)	21.56	10.01	8.79
95% CL	5.93	6.63	7.9
$k_{of}^a \times 10^3$ [m ³ / (kg of catalyst·s)]	0.043	0.54	0.026
95% CL $\times 10^3$	0.004	0.05	0.003
	$\alpha = 0.022$ (95% CL of 0.014)		

^a Preexponential factor as obtained from eq 9; unit for second order (m⁶/kg of catalyst·s).

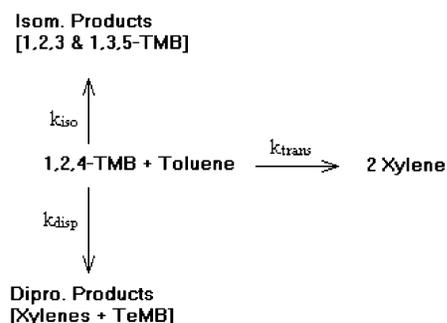
is observed that the amount of 1,3,5-TMB formed during the reaction of 1,2,4-TMB alone was about 2 times higher than the amount formed during transalkylation reaction. The highest 1,3,5-TMB yield was found to be approximately 6.2 wt % at 38% conversion of 1,2,4-TMB, compared to 3.5 wt % for the transalkylation reaction. The situation is similar for 1,2,3-TMB and TeMB yields, where higher amounts are obtained with pure trimethylbenzene reaction compared to the amount formed when the trimethylbenzene is blended with toluene (Tables 2 and 3). This can be explained by the nature of the transalkylation reaction where 1 mol of 1,2,4-TMB reacts with 1 mol of toluene to produce 2 mol of xylenes. This is in contrast to disproportionation of 1,2,4-TMB that produces 1 mol each of xylene and tetramethylbenzenes.

3.4.6. Xylene to Tetramethylbenzene Ratio. Figure 8 shows xylene-to-tetramethylbenzene (X/TeMB) distributions at various conversion levels over the FCC-Y catalyst. The X/TeMB ratio for the transalkylation reaction is about 7 times higher than that of the pure 1,2,4-TMB reaction. This gives further evidence that transalkylation of trimethylbenzene with toluene boosts

Table 6. Correlation Matrix for Parameters: TOS Model

	k_{0trans}	E_{trans}	k_{0iso}	E_{iso}	k_{0disp}	E_{disp}	α
k_{0trans}	1.0000	-0.1594	0.5547	0.0196	0.3657	0.0318	0.8069
E_{trans}	-0.1594	1.0000	0.0163	-0.2017	0.0456	-0.4443	-0.0108
k_{0iso}	0.5547	0.0163	1.0000	-0.0570	0.3918	0.0033	0.7799
E_{iso}	0.0196	-0.2017	-0.0570	1.0000	0.0131	-0.3247	0.0048
k_{0disp}	0.3657	0.0456	0.3918	0.0131	1.0000	-0.0244	0.6896
E_{disp}	0.0318	-0.4443	0.0033	-0.3247	-0.0244	1.0000	-0.0142
α	0.8069	-0.0108	0.7799	0.0048	0.6896	-0.0142	1.0000

Scheme 1



xylene production significantly. The above discussion on the nature of the transalkylation reaction also applies to the X/TeMB scenario.

4. Kinetic Modeling

4.1. Model Formulation. The experimental results were modeled using steady-state approximations with catalyst decay to be a function of time on stream. To develop a suitable kinetic model representing the overall transformation of 1,2,4-TMB, the reaction network shown in Scheme 1 is used.

The following set of species balances and catalytic reactions can be written:

$$\frac{V}{W_c} \frac{dC_{124-TMB}}{dt} = -[k_{iso}C_{124-TMB} + 2k_{disp}C_{124-TMB}^2 + k_{trans}C_{tol}C_{124-TMB}] \exp[-\alpha t] \quad (1)$$

$$\frac{V}{W_c} \frac{dC_{tol}}{dt} = -[k_{trans}C_{124-TMB}C_{tol}] \exp[-\alpha t] \quad (2)$$

$$\frac{V}{W_c} \frac{dC_{iso}}{dt} = k_{iso}C_{124-TMB} \exp[-\alpha t] \quad (3)$$

$$\frac{V}{W_c} \frac{dC_{disp}}{dt} = k_{disp}C_{124-TMB}^2 \exp[-\alpha t] \quad (4)$$

where C_{tol} is the toluene concentration in the riser simulator, $C_{124-TMB}$ is the 1,2,4-TMB concentration in the riser simulator, V is the volume of the riser (45 cm³), W_c is the mass of the catalyst (0.81 g of catalyst), t is the time (s), α is the deactivation constant, and k is the rate constant (cm³/(g of catalyst·s)).

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

1. The isomerization of 1,2,4-TMB follows simple first-order kinetics, whereas disproportionation is second order as proposed by Atias et al.⁹ and Ko and Kuo.²¹

2. An irreversible reaction path is assumed for both the isomerization and disproportionation reaction.

3. Tetramethylbenzenes are entirely the results of the disproportionation reaction. [The disproportionation reaction in-

volves the formation of 1 mol of xylenes and 1 mol of tetramethylbenzenes from 2 mol of 1,2,4-TMB.]

4. Toluene disproportionation reaction is negligible due to the very small amount of benzenes observed in the product mixture.

5. A single deactivation function is defined for all the reactions taking place.

6. Dealkylation reaction is inconsequential due to the minor amounts of gases in the reaction system.

7. The reactor operates under isothermal conditions, justified by the negligible temperature change observed during the reactions.

Using similar derivation procedures outlined in refs 9 and 22, eqs 1–4 can be expressed in terms of weight fractions which are the measurable variables from GC analysis as

$$\frac{dy_A}{dt} = -[k_{iso}y_A + 2v_Ak_{disp}y_A^2 + v_Bk_{trans}y_Ay_B] \frac{W_c}{V} \exp[-\alpha t] \quad (5)$$

$$\frac{dy_B}{dt} = -v_Ak_{trans}y_Ay_B \frac{W_c}{V} \exp[-\alpha t] \quad (6)$$

$$\frac{dy_C}{dt} = v_1k_{iso}y_A \frac{W_c}{V} \exp[-\alpha t] \quad (7)$$

$$\frac{dy_D}{dt} = v_Dk_{disp}y_A^2 \frac{W_c}{V} \exp[-\alpha t] \quad (8)$$

where “A”, “B”, “C”, and “D” represent the reactant 1,2,4-TMB, the reactant toluene, the reaction products 1,2,3-TMB + 1,3,5-TMB, and TeMBs, respectively. Also

$$v_A = \frac{W_{hc}}{MW_{TMB}V} \quad v_B = \frac{W_{hc}}{MW_{tol}V}$$

$$v_1 = \frac{MW_{TMB}}{MW_{TMB}} = 1 \quad v_D = \frac{W_{hc}MW_{TeMB}}{MW_{TMB}^2V}$$

where W_{hc} = total mass of hydrocarbons inside the riser (0.162 g) and MW_X = molecular weight of X molecule.

Kinetic constants for transalkylation, isomerization, and disproportionation can be expressed using the Arrhenius equation, and a centering temperature T_0 is the average reaction temperature introduced to reduce parameter interaction.

$$k_i = k_{0i} \exp\left(\frac{-E_i}{R} \left[\frac{1}{T} - \frac{1}{T_0}\right]\right) \quad (9)$$

4.2. Discussion of Kinetic Modeling Results. The kinetic parameters k_{0i} , E_i , and α for the transalkylation reaction were obtained using nonlinear regression (MATLAB package). Table 5 reports the parameters obtained along with the corresponding 95% confidence limits, while Table 6 presents the correlation

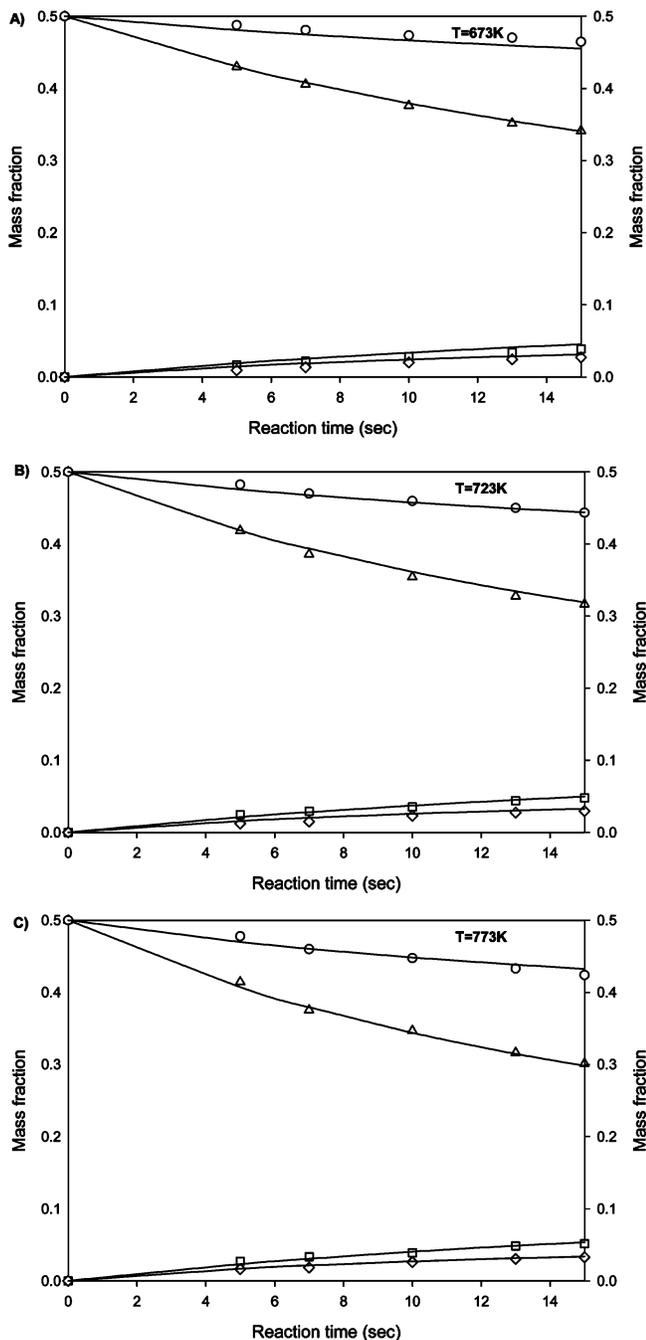


Figure 9. Comparison between experimental results and numerical simulations (—) based on reaction network (Scheme 1) for 1,2,4-TMB transalkylation reaction with toluene at (A) $T = 673$ K, (B) $T = 723$ K, and (C) $T = 773$ K. (○) Toluene; (△) 1,2,4-TMB; (□) isomerization products [1,2,3- and 1,3,5-TMB]; (◇) disproportionation product [TeMB].

matrix for the parameters. From the results of the kinetic parameters presented in Table 5, it is observed that catalyst deactivation was found to be small, $\alpha = 0.022$, indicating low coke formation in agreement with the data shown in Table 4 indicating very low coke yield. Apparent activation energies of 21.56, 10.01, and 8.79 kJ/mol were obtained for the transalkylation, isomerization, and disproportionation reactions of 1,2,4-TMB, respectively. The correlation matrix of the regression analysis shows that the parameters are highly correlated.

Atias et al.⁹ reported an apparent energy of activation of 19.7 kJ/mol for the isomerization reaction of 1,2,4-TMB over USY zeolite, and a value of 6.7 kJ/mol for the disproportionation reaction. These values are in agreement, or have the same order with the values obtained in the present study despite our

differences in conversion. However, values of our activation energies are generally lower than those reported by Ko and Kuo,²¹ who observed activation energies of 37.4 and 46.6 kJ/mol for isomerization of 1,2,4-TMB over HY zeolite to form 1,2,3-TMB and 1,3,5-TMB, respectively. They also reported activation energies of 30.8 and 21.6 kJ/mol for the formation of 1,2,3,4-TeMB and (1,2,3,5 + 1,2,4,5)-TeMB, respectively. Ko and Kuo²¹ investigations were carried out in a fixed-bed reactor at much lower temperatures of 200–300 °C.

Comparing the apparent activation energy values determined, it was observed that the isomerization of 1,2,4-TMB (E_{iso}) involves a higher apparent energy of activation compared to the disproportionation reaction (E_{disp}). This is in agreement with the findings of refs 9 and 21, in which the authors reported similar trends for the transformation reaction of 1,2,4-TMB over USY as discussed above.

The apparent activation energy (E_{trans}) of 21.56 kJ/mol was obtained for the toluene disappearance during the transalkylation reaction over the FCC-Y catalyst. We have not come across any reported value in the literature to compare with our value.

To check the validity of the estimated kinetic parameters for use at conditions beyond those of the present study, the fitted parameters were substituted into the comprehensive model developed for this scheme and the equations were solved numerically using the fourth-order Runge–Kutta routine. The numerical results were compared with the experimental data as shown in Figure 9. It can be observed from this figure that the calculated results compare very well with the experimental data.

5. Conclusions

The following conclusions can be drawn from the transalkylation reaction of 1,2,4-TMB with toluene over the FCC-Y zeolite catalyst and the subsequent comparison with the reactions of pure toluene and 1,2,4-TMB under similar conditions.

1. The reactivity of 1,2,4-TMB was only enhanced slightly during the transalkylation reaction with toluene. However, toluene that was found almost inactive¹⁰ became reactive upon blending with 1,2,4-TMB. Since a very negligible amount of toluene was found during the transformation reaction of 1,2,4-TMB alone, the reactivity of toluene can only be attributed to the transalkylation reaction.

2. The results show that thermodynamic equilibrium compositions of aromatics during transalkylation reaction are governed by the methyl groups per benzene ring (M/R) of the feedstocks, which is consistent with previous studies.

3. The transalkylation reaction of 1,2,4-TMB with toluene consistently gave higher xylene yield and higher P/O and X/TeMB ratios, but lower 1,3,5-TMB/1,2,3-TMB ratio and lower 1,2,3-TMB, 1,3,5-TMB, and TeMB yields, than those of the pure 1,2,4-TMB reaction.

4. Kinetic parameters for the 1,2,4-TMB–toluene system during their transformation reactions via transalkylation, isomerization, and disproportionation products have been calculated using the catalyst activity decay function based on time on stream (TOS). The apparent activation energies were found to decrease as follows: $E_{\text{transalkylation}} > E_{\text{isomerization}} > E_{\text{disproportionation}}$.

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Nomenclature

C_i = concentration of species i in the riser simulator (mol/m³)

CL = confidence limit

E_i = apparent activation energy of i th reaction (kJ/mol)

k = apparent kinetic rate constant [m³/(kg of catalyst·s)] = $k'_0 \exp(-E_R/R)[(1/T) - (1/T_0)]$

k'_0 = preexponential factor in Arrhenius equation defined at an average temperature [m³/(kg of catalyst·s)], units based on first-order reaction

MW _{i} = molecular weight of species i

r = correlation coefficient

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 cm³)

W_c = mass of catalyst (0.81 g of catalyst)

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

y_i = mass fraction of i th component (wt %)

Greek Symbol

α = apparent deactivation constant (s⁻¹) (TOS model)

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