

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/216868584>

Transformation of Toluene and 1,2,4-Trimethylbenzene over ZSM-5 and Mordenite Catalysts: A Comprehensive Kinetic Model with Reversibility

ARTICLE in INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · JULY 2010

Impact Factor: 2.59 · DOI: 10.1021/ie100527x

CITATIONS

16

READS

77

3 AUTHORS, INCLUDING:



Abdullah M. Aitani

King Fahd University of Petroleum and Min...

108 PUBLICATIONS 729 CITATIONS

SEE PROFILE



Sulaiman al-khattaf

King Fahd University of Petroleum and Min...

117 PUBLICATIONS 1,118 CITATIONS

SEE PROFILE

Transformation of Toluene and 1,2,4-Trimethylbenzene over ZSM-5 and Mordenite Catalysts: A Comprehensive Kinetic Model with Reversibility

S. M. Waziri, A. M. Aitani, and S. Al-Khattaf*

Center of Research Excellence in Petroleum Refining & Petrochemicals, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

The catalytic transformations of toluene, 1,2,4-trimethylbenzene (TMB), and an equimolar mixture of the two compounds were investigated over H-mordenite and H-ZSM-5 catalysts. A series of experiments were conducted in a riser simulator over a temperature range of 300–400 °C and reaction times of 5–20 s. The influence of reaction conditions on variation of 1,2,4-TMB conversion, toluene conversion, para- to ortho-xylene ratio, xylenes to TMB isomers ratio, 1,3,5-TMB to 1,2,3-TMB ratio, and xylenes to benzene ratio were discussed. The study also includes the development of comprehensive kinetic models for isomerization, disproportionation, and transalkylation reactions of 1,2,4-TMB and toluene. The models account for reversibility of the isomerization reaction based on values of temperature dependent thermodynamic equilibrium constants. Catalysts deactivation was modeled using an activity decay function based on time-on-stream (TOS). The developed models gave a good match with experimental data based on a statistically significant estimate of the kinetic parameters in the models. For the 1,2,4-TMB reaction and transalkylation of 1,2,4-TMB with toluene, the apparent activation energy over H-ZSM-5 was higher than that over H-mordenite (i.e., $E_{app,(H-ZSM-5)} > E_{app,(H-Mordenite)}$) while the reverse order was observed for the toluene reaction over the two catalysts. A simple correlation that gives accurate representation of the temperature dependency of thermodynamic equilibrium compositions of TMB isomers was also reported.

I. Introduction

Xylenes are important basic raw materials with considerable application in the chemicals and petrochemicals industry. The para isomer is used as a raw material in the production of polyester fibers, resins, and other useful products. Catalytic reforming and steam cracking of naphtha are the principal sources of xylenes, along with benzene and toluene. However, because of thermodynamic constraints, the product yields from these sources (BTX percentage: 32:36:32, respectively) give lower amounts of the more valuable xylenes compared to the less demanded toluene.¹ The mismatch between production and actual market demand for different aromatics is met by converting toluene and heavy aromatics into xylenes using processes such as disproportionation and transalkylation. The source of such heavy aromatics is usually heavy reformate streams or pyrolysis gasoline. 1,2,4-TMB is usually used as a model compound in most transalkylation studies since it represents more than 40 wt % of C₉ aromatics in heavy reformate.

Activity and selectivity of catalysts in the transformations of TMBs are significantly influenced by the dimensions and the pore structure of the catalysts. The application of zeolites as shape selective catalysts for alkylation reactions has been well-documented in comprehensive reviews on the subject such as Čejka and Wichterlova² and Tsai et al.³ Industrial processes, such as Tatoray and TransPlus, utilize large pore zeolite catalysts to favor greater diffusivity of large aromatic (C₉ and C₁₀) molecules that are involved in the transalkylation reactions.³ Nickel impregnated with mordenite or exchanged over dealuminated mordenite is one of the popular catalysts used in these processes. Several zeolite-based catalysts have been reported in laboratory studies on the transformation of toluene and TMBs. These include zeolites of L,⁴ Y,^{4,5} and beta types,^{4,6,7} ZSM-5,⁸

ZSM-12,³ MCM-41,⁹ NU-87,¹⁰ SAPO-5,¹¹ and mordenite.^{12–14} Metals, such as Cu, Ni, Pt, Mo, Re, etc., are often incorporated into the zeolite catalysts to hydrogenate polyaromatics coke precursors during heavy aromatics transalkylation and thus reduce the problem of catalyst aging.¹⁵ Zeolites with small and medium pores such as ZSM-5 and MCM-22 are not very suitable for disproportionation and transalkylation of TMB or higher aromatic hydrocarbons because of pore size limitation which force these zeolites to act only by the external active sites.⁴

Although toluene disproportionation can also be catalyzed by large-pore zeolites, industrial processes mostly utilize 10-ring zeolites having a medium-pore size such as ZSM-5 zeolite.³ Roger et al.⁸ investigated the reaction network of 1,2,4-TMB disproportionation over medium pore ZSM-5 zeolite. They found that isomerization of 1,2,4-TMB to 1,2,3- and 1,3,5-TMB isomers was 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 also 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 diffusion resistances by pore mouth narrowing favored the paring reaction inside the zeolite crystals. Čejka et al.⁴ noted that diffusion of TMBs into the ZSM-5 zeolite channel system is rather slow, and the conversions of TMBs are usually significantly lower compared to large pore zeolites because of significant steric constraints for the large TMBs molecules. Park and Rhee¹⁰ conducted a study on the catalytic activity and selectivity of medium pore zeolite NU-87 in the conversion of 1,2,4-TMB. The authors showed that for the smallest TMB isomer, 1,2,4-TMB, used as a reactant, the disproportionation reaction took place in the channel system of the zeolite in contrast to the transformation of 1,3,5- and 1,2,3-TMBs, which reacted mainly on the external surface.

* To whom correspondence should be addressed. Tel.: +966-3-860-1429. Fax: +966-3- 860-4234. E-mail: skhattaf@kfupm.edu.sa.

The transformation of TMBs over large pore zeolites, such as for zeolites Y, beta, and mordenite, proceeds mainly in the zeolite channel system. Thus, the rate of the reaction is much higher compared to that of medium pore zeolites. Čejka et al.¹⁶ have attributed this difference to the possibility to accommodate higher concentrations of reactants inside the channel system, which leads to an increase in the rate of bimolecular reaction. Das et al.¹⁵ studied the transformation reactions of toluene and TMB using zeolite beta. Highest yield of xylenes was obtained at a temperature of 400 °C and toluene/TMB molar ratio of about 1:1. Chu and Chen¹⁷ used zeolite beta to investigate the effect of Si/Al ratios on TMB transformation. At low Si/Al ratios TMB disproportionation was favored in contrast to high Si/Al ratios, which favored the isomerization reaction. Mikhail et al.¹⁸ reported xylene yield between 17 and 35% using Pt/La–Y zeolite at 400 °C. TMB conversion differed according to the isomer used in the sequence 1,2,4-TMB > 1,3,5-TMB > 1,2,3-TMB. A similar sequence of reactivity of the TMB isomers was reported by Dumitriu et al.¹¹ using SAPO-5 catalyst. It was found that the strength of acid sites influences the competition among various reactions that occur in the transalkylation process. In general, the transalkylation and/or disproportionation reactions occur on stronger acid sites, while the isomerization of xylenes and TMBs predominates on weaker acid sites.

The above literature overview shows that the majority of studies on transformations of toluene, 1,2,4-TMB and their transalkylation reaction are related to catalyst development. Most of the studies were carried out in fixed-bed reactor, and less attention was paid to kinetic studies. Therefore, the present study focuses on the development of a detailed kinetic model which accounts for all important reactions involved in the transformation of toluene, 1,2,4-TMB, and their transalkylation reaction. This study was carried out using H-mordenite (H-M) and H-ZSM-5 (H-Z) catalysts in a riser simulator reactor. The kinetic model developed in this study addresses the issue of the reversible nature of the isomerization reaction of 1,2,4-TMB which has not hitherto been adequately considered in other studies. In addition to kinetic modeling, the study highlights the effect of reaction conditions (time, temperature, and conversion) on the para to ortho xylene ratio, xylenes to TMB isomers ratio, xylenes to TMB ratio, and 1,3,5-TMB to 1,2,3-TMB ratio.

2. Experimental Section

2.1. The Riser Simulator. All experimental runs were carried out in a 45 cm³ riser simulator. This reactor is novel bench-scale equipment with an internal recycle unit invented by de Lasa.¹⁹ A comprehensive description of the reactor has been given elsewhere.²⁰ 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 reactor was designed with an impeller located in its upper section that provides a fluidized-bed of catalyst particles as well as an intense gas mixing inside the reactor.

2.2. Materials. H-mordenite (H-M) zeolite was obtained from Tosoh Company, Japan, with a SiO₂/Al₂O₃ molar ratio of 135.9. H-ZSM-5 (H-Z) zeolite with a SiO₂/Al₂O₃ molar ratio of 29.4 was obtained from CATAL, U.K. Analytical grade (99% purity) 1,2,4-TMB and toluene were obtained from Sigma-Aldrich. All chemicals were used as received as no attempt was made to further purify the samples.

2.3. Catalyst Characterization. The surface area of the catalysts was measured by nitrogen adsorption at –196 °C using a NOVA 1200 Porosimeter from Quantachrome. The concentra-

Table 1. Catalyst Characterization Results

property	ZSM-5 (H-Z)	Mordenite (M-Z)
total pore volume (cm ³ /g)	0.13	0.16
BET surface area (m ² /g)	295	411
SiO ₂ /Al ₂ O ₃ (molar ratio)	29.4	135.9
total acidity (mmol/g)	0.5	0.15
Lewis acid sites (%)	68	80
Bronsted acid sites (%)	32	20

tion and type of acid sites were determined by adsorption of pyridine as probe molecules followed by FTIR spectroscopy (Nicolet 6700 FTIR) using the self-supported wafer technique.

2.4. Procedure. Catalytic experiments were carried out using H-M and H-Z catalysts in the riser simulator with a catalyst/reactant ratio of 5 (mass of catalyst = 0.81 g, mass of reactant injected = 0.162 g). A total of 72 runs were conducted at the following reaction conditions; temperatures of 300, 350, and 400 °C and contact times of 5, 10, 15, and 20 s. Half of the runs were done using the H-M catalyst while the remaining tests were performed using the H-Z catalyst. For each catalyst, the tests were done with three different feeds: toluene, 1,2,4-TMB, and an equimolar mixture of 1,2,4-TMB and toluene (equivalent to 56.6 wt % 1,2,4-TMB, 43.4 wt % toluene). The heating of the riser simulator was conducted under a continuous flow of inert gas (Ar). The temperature controller and timer were used to maintain the reaction at the desired reaction temperature and contact time, respectively. The conversion of toluene and 1,2,4-TMB is defined as follows:

$$\text{conversion of toluene} = \frac{([\text{toluene}]_{\text{feed}} - [\text{toluene}]_{\text{product}})/[\text{toluene}]_{\text{feed}} \times 100}$$

$$\text{conversion of 1,2,4-TMB} = \frac{([1,2,4\text{-TMB}]_{\text{feed}} - [1,2,4\text{-TMB}]_{\text{product}})/[1,2,4\text{-TMB}]_{\text{feed}} \times 100}$$

2.5. Analysis. 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 reaction products were analyzed in an Agilent 6890N gas chromatograph with a flame ionization detector and an HP-INNOWAX capillary column (60 m cross-linked polyethylene glycol with an internal diameter of 0.32 mm). Reproducibility checks on the experimental results show that typical errors were in the range of ±2%.

3. Results and Discussion

3.1. Catalyst Characterization. The textural properties of H-M and H-Z catalysts are presented in Table 1. The two catalysts exhibited typical textural properties with a total pore volume of 0.13 and 0.16 cm³/g, respectively. The BET surface area of H-M catalyst was 411 m²/g and that of H-Z was 295 m²/g. The total acidity of the H-Z catalyst was 3.3 times higher than the H-M catalyst.

3.2. Reaction of Toluene. The major products from the reaction of toluene over both H-M and H-Z catalysts were found to be *para*-xylene, *ortho*-xylene, *meta*-xylene, and benzene. Figure 1b shows the effect of temperature and reaction time on toluene conversion over the two catalysts. The results clearly indicate that conversion of toluene increases with increasing temperature and contact time. At all the conditions depicted in Figure 1b, the H-M catalyst appears to be a more active catalyst for the conversion of toluene compared to H-Z. This is similar to what was observed in the transformation of 1,2,4-TMB.

Comparison between the results in parts a and b of Figure 1 highlights a significant difference in the reactivity of toluene

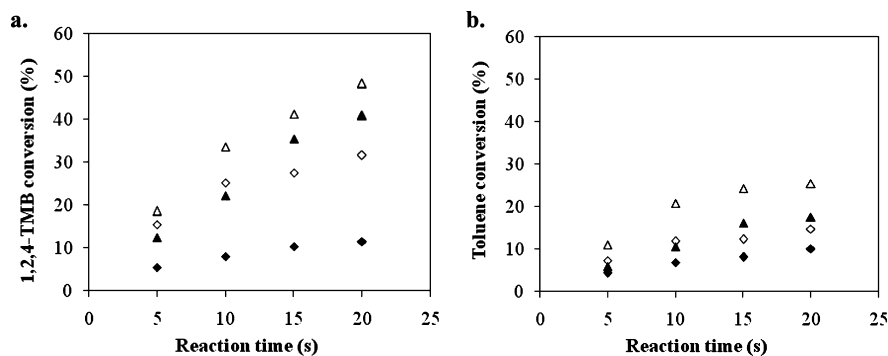


Figure 1. Relationship between conversion and reaction time over H-mordenite (Δ , \blacktriangle) and H-ZSM-5 (\diamond , \blacklozenge) for (a) reaction of 1,2,4-TMB and (b) reaction of toluene. White symbols represent data at 300 °C, while black symbols are for data at 400 °C.

and 1,2,4-TMB over the two catalysts. In all the conditions investigated, 1,2,4-TMB turned out to be a more reactive substrate than toluene. For example, at 400 °C and reaction time of 20 s, the conversion of toluene over the H-M catalyst was 25.3%, while the conversion of 1,2,4-TMB under the same conditions was 48.3%. Similarly, at a temperature of 400 °C and reaction time of 20 s, conversions of 14.6% and 31.6% were observed for toluene and 1,2,4-TMB, respectively, over the H-Z catalyst.

Thermodynamic calculations show that the equilibrium mixture formed by disproportionation of toluene contains significant proportions of TMBs and TeMBs.²¹ However, results obtained in our study show that over the H-Z catalyst, this reaction proceeds almost quantitatively to benzene plus xylenes and very negligible amount of higher alkylated aromatics. As suggested by Olson and Haag,²² the absence of TMBs and TeMBs products in ZSM-5 was due to transition state selectivity, which prohibits formation of these bulky products.

3.3. Reaction of 1,2,4-TMB. The transformation of 1,2,4-TMB was investigated over H-Z and H-M catalysts at 300, 350, and 400 °C for residence times of 5, 10, 15, and 20 s. For both catalysts, the major products were found to be *para*-xylene, *ortho*-xylene, *meta*-xylene, 1,3,5-TMB, 1,2,3-TMB, and tetramethylbenzenes (TeMBs). The influence of reaction time and temperature on the conversion of 1,2,4-TMB over H-M and H-Z can be seen in Figure 1a. It is evident from the results that the conversion increases with both reaction time and temperature. However, at all reaction conditions it was observed that H-M gave a higher level of conversion compared to the H-Z catalyst. For instance, as can be seen in Table 2, at 400 °C and 20 s the conversion level over H-M was 48.3% while that over H-Z was 31.6%.

3.4. Reaction of 1,2,4-TMB and Toluene. Figure 2 shows a list of reactions occurring during the transformation of 1,2,4-TMB in the presence of toluene. The primary reaction is the transalkylation reaction of 1,2,4-TMB and toluene which leads to the formation of xylenes. The major products of the reaction were similar to those obtained using 100% 1,2,4-TMB as feed, i.e., *para*-xylene, *ortho*-xylene, *meta*-xylene, 1,3,5-TMB, 1,2,3-TMB, and TeMBs. Benzene concentrations in the product stream were in the range of 0.3–2.0%, which is in contrast to the results obtained with 1,2,4-TMB where the highest benzene concentration was 0.1%.

The influence of reaction conditions on the conversions of 1,2,4-TMB and toluene is presented in parts a and b of Figure 3. The results show that both conversions increase with increasing reaction time and temperature. It is clear from the results that the conversion of 1,2,4-TMB is higher than the conversion of toluene for all the experimental points considered

Table 2. Summarized Experimental Results at Reaction Temperature of 400 °C and Reaction Time of 20 s

catalyst	ZSM-5 (H-Z)			Mordenite (H-M)		
feed composition (mol %)						
toluene/1,2,4-TMB	100:0	0:100	50:50	100:0	0:100	50:50
Conversion (wt %)						
toluene	14.6		20.8	25.3		28.8
1,2,4-TMB		31.6	36.6		48.3	49.1
Yield on Feed (wt %)						
light gases	0.0	0.4	0.2	0.0	0.2	0.1
benzene	6.6	0.0	2.3	11.8	0.1	2.0
toluene	85.4	1.0	34.3	74.7	2.1	30.9
xylenes (total)	7.7	5.5	13.8	12.5	14.1	27.4
<i>p</i> -xylene	2.1	1.3	3.6	3.1	3.3	6.6
<i>m</i> -xylene	4.0	2.7	7.0	6.6	7.4	14.4
<i>o</i> -xylene	1.6	1.5	3.2	2.8	3.4	6.4
1,3,5-TMB	0.1	12.3	7.4	0.3	9.0	5.1
1,2,4-TMB	0.2	68.4	35.9	0.7	51.7	28.8
1,2,3-TMB	0.0	6.4	3.7	0.1	3.2	1.9
TeMB	0.0	5.7	1.3	0.0	17.6	3.2
Selectivity, mol/mol						
<i>p</i> -xylene/ <i>o</i> -xylene	1.33	0.83	1.13	1.13	0.97	1.05
xylenes/TeMB		1.23	13.50		1.02	10.79
1,3,5-TMB/1,2,3-TMB		1.92	1.99	2.73	2.79	2.71

in this study. At 400 °C, the conversion of toluene rose from 7.6% at 5 s to 28.8% at 20 s while conversion of 1,2,4-TMB increases from 22.1% at 5 s to 49.1 at 20 s over the mordenite catalyst. Although the change of conversion with reaction time and temperature were found to follow similar trends over both catalysts, the conversion levels obtained with H-Z are smaller than those observed using H-M.

3.5. Effect of Nature of Feed and Catalyst. 3.5.1. Product Selectivity. The major products in the transformation of toluene and 1,2,4-TMB are xylenes, benzene, TMBs, and TeMBs. A comparison between the selectivity of these products over ZSM-5 catalyst is presented in Figure 4 at a reaction time of 20 s and 400 °C. The selectivity values calculated as follows:

$$S_i = \frac{y_i}{y_{\text{benzene}} + y_{\text{xylenes}} + y_{\text{isoTMB}} + y_{\text{TeMB}}} \times 100$$

where y_i stands for the weight fraction of component i in the product mixture. The figure indicates that the production of xylenes via the disproportionation of toluene results in the formation of a large amount of benzene as a byproduct with very little amounts of higher alkylbenzenes. Using 1,2,4-TMB as feed to produce xylenes gave substantial amounts of higher alkyl benzenes at the expense of benzene which was produced in trace amounts. It can be noticed that the amount of isomerization products formed when 1,2,4-TMB was used as

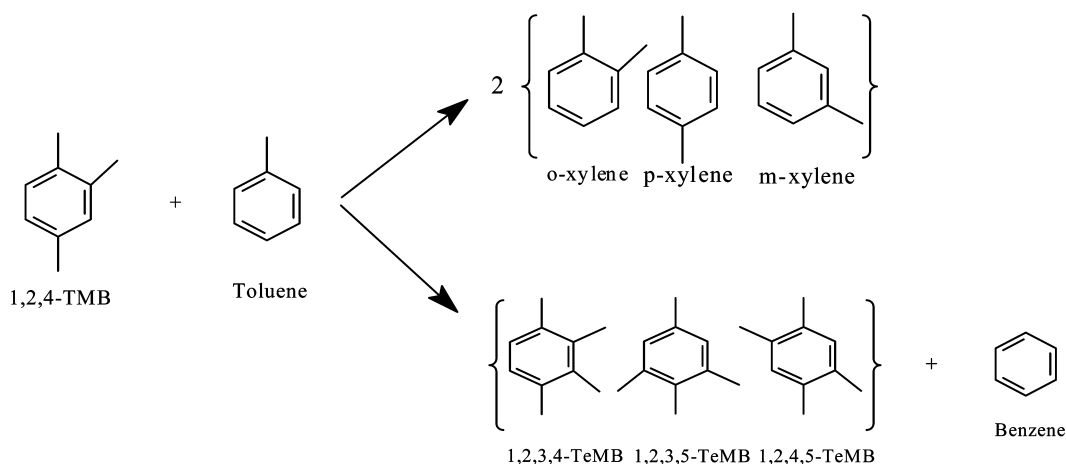
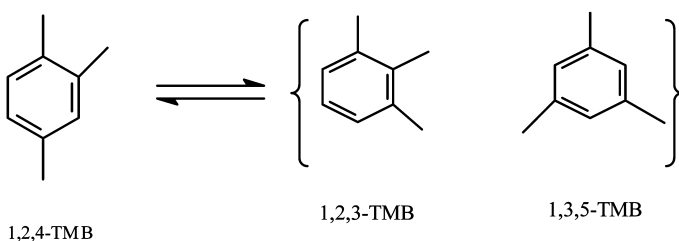
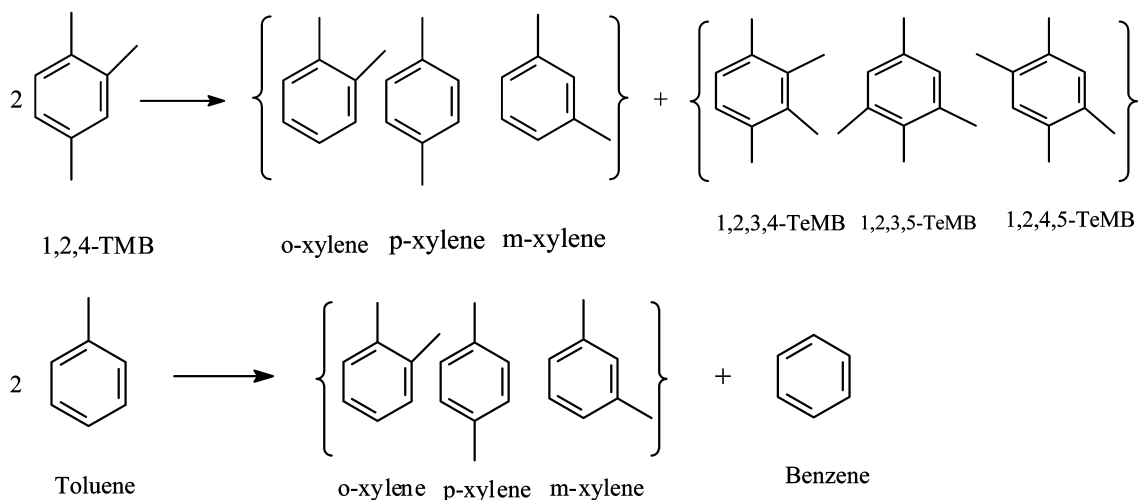
(A) Transalkylation Reactions**(B) Isomerization of 1,2,4-TMB****(C) Disproportionation Reactions**

Figure 2. Reactions occurring during 1,2,4-TMB disproportionation and transalkylation with toluene.

feed was about 3 times of the amount of xylenes formed. However, using an equimolar blend of toluene and 1,2,4-TMB as feed produced both benzene and higher alkyl benzenes as products. A closer look at the results reveals that blending of toluene and 1,2,4-TMB as feed leads to dramatic enhancement in xylenes yield compared to when either of the feed components was used. In other words, transalkylation of toluene and 1,2,4-TMB is more selective for xylene production than toluene or 1,2,4-TMB disproportionation. This enhancement in xylene yield can be attributed to an increase in the methyl to benzene ring ratio (M/R) that

result from blending of toluene with heavy aromatics. The results show that the degree of enhancement in xylenes selectivity is greater over H-M compared to H-Z.

3.5.2. 1,3,5-TMB to 1,2,3-TMB Ratio. Table 2 presents a summary of experimental results obtained at a reaction time of 20 s and temperature of 400 °C. The table shows conversion, yields, and selectivity values for different combinations of feeds and catalyst systems. The values of 1,3,5-TMB to 1,2,3-TMB ratios were relatively higher over H-M (~2.7) in comparison to H-Z (~2.0). This difference is not unexpected because H-Z

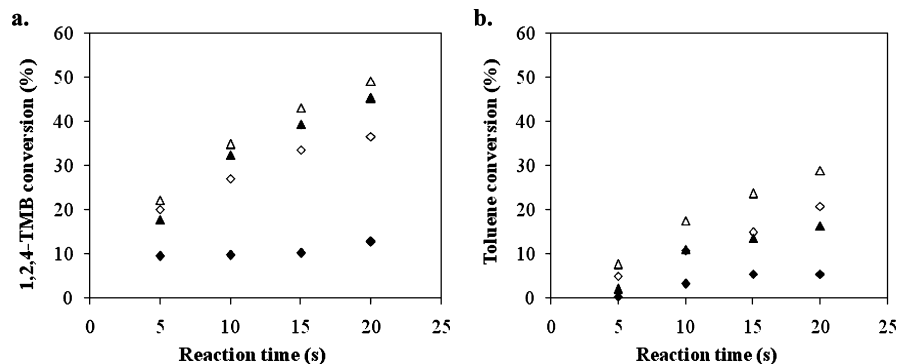


Figure 3. Relationship between conversion and reaction time over H-mordenite (Δ, \blacktriangle) and H-ZSM-5 (\diamond, \blacklozenge) for transalkylation reaction of 1,2,4-TMB with toluene. White symbols represent data at 300 °C, while black symbols are for data at 400 °C.

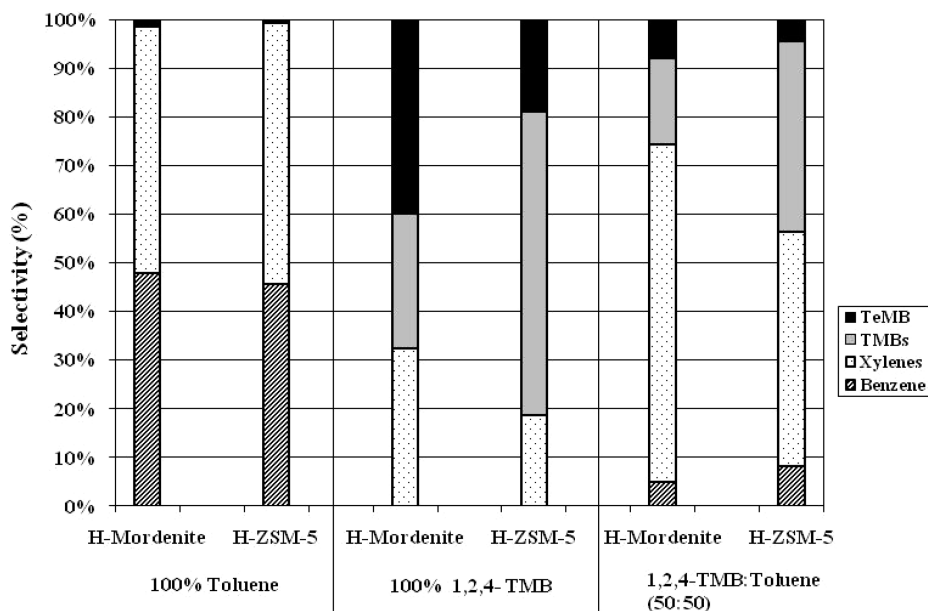


Figure 4. Comparison between values of selectivity of reaction products over (a) H-ZSM-5 and (b) H-mordenite. Reaction time, 20 s; reaction temperature, 400 °C.

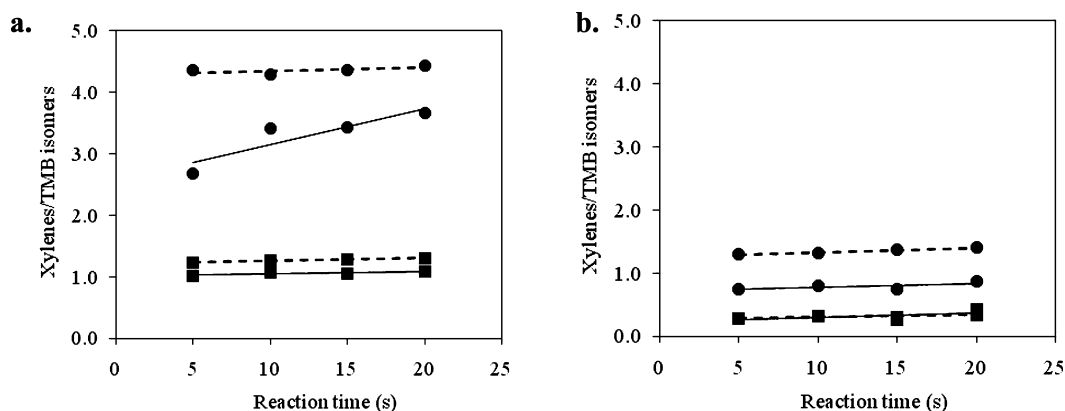


Figure 5. Comparisons of the xylenes/TMB isomers ratio (mol/mol) between transformation of 1,2,4-TMB (\blacksquare) and an equimolar mixture of 1,2,4-TMB and toluene (\bullet) over (a) H-mordenite and (b) H-ZSM-5. Reaction temperature, 300 °C (solid lines); 400 °C (dashed lines).

is a two-dimensional 10-ring pore zeolite while H-M is a one-dimensional large pore zeolite. It is known that zeolites with large cages generally favor the formation of the larger 1,3,5-TMB molecule, while small-pore zeolites favor the 1,2,3-TMB isomer. The thermodynamic equilibrium value of the TMB isomers at 400 °C was reported to be 124:135:123 = 67.11:25:7.89%,²³ which implies that the value of 1,3,5-TMB/1,2,3-

TMB ratio at equilibrium is 3.2. These results indicate that shape selectivity does play a significant role in the product distribution of TMB isomers. Wang et al.⁷ reported a value of 2.7 for the 1,3,5-/1,2,3-TMB ratio at 348 °C over USY-zeolite, while Park and Rhee¹⁰ reported a ratio of 1,3,5-/1,2,3-TMB as 1.99 over NU-87 zeolite with catalytic properties falling between those of medium- and large-pore zeolites.

3.5.3. *para*-Xylene to *ortho*-Xylene (P/O) Ratio. The variation of P/O ratio with reaction time for the transformations of toluene, 1,2,4-TMB, and a mixture of 1,2,4-TMB and toluene shows that over the H-M catalyst the P/O ratios have values close to the thermodynamic equilibrium value of unity at most of the experimental conditions. However, exceptions to these were seen for 1,2,4-TMB reaction (P/O ~ 0.6) at 300 °C and that of toluene (P/O ~ 2.6) at 300 °C. It is clear that for the toluene reaction, low temperature leads to P/O ratios in excess of the equilibrium value while the reverse situation is true in the case 1,2,4-TMB transformation. The formation of excess *para*-xylene over H-Z arises from the slow transport of the *ortho*- and *meta*-isomers due to diffusional restriction. It is also not surprising that most of the P/O ratios are close to the thermodynamic equilibrium values over the large-pore H-M catalyst. This is because H-M allows the isomers to freely move without diffusional constraints.

3.5.4. Xylenes to TMB Isomers Ratio. Xylenes yield relative to isomerization products is an important performance index because xylenes are the main products of interest. The ratio of xylenes to 1,2,3-TMB and 1,3,5-TMB isomers, hereafter referred to as the xylenes/TMB isomers ratio, is presented in parts a and b of Figure 5 under different reaction conditions. The results in both figures show that there is a tremendous difference in the value of the xylenes/TMB ratio between the case where 1,2,4-TMB was used as feed and the case where it was blended with toluene. Figure 5a shows that by using 1,2,4-TMB as feed over the H-M catalyst, the ratio ranges between 1.0 and 1.3. However, cofeeding equimolar amounts of 1,2,4-TMB and toluene can make the ratio increase by as much as 3.5 times. This dramatic increase is not only as a result of increase in xylene yields but also due to a simultaneous decrease in the TMB isomers when 1,2,4-TMB is blended with toluene.

3.5.5. Xylenes to Benzene Ratio. The choice of feed had a significant effect on the value of the xylenes/benzene ratio. Changing the feed from toluene to 50:50 molar blend of toluene and 1,2,4-TMB brings about a tremendous increase in the ratio. On both H-Z and H-M, the xylenes/benzene ratio exhibits a value close to 1.0 when the feed is toluene, while the use of the equimolar mixed feed gives values that are much higher than 1.0. As shown in Scheme 1, the disproportion of toluene involves the formation of equal molar amounts of benzene and xylenes from two molecules of toluene. Thus, values close to the stoichiometric ratio of unity suggest absence of secondary transalkylation and dealkylation reactions. The results show that the H-M catalyst gave higher values of the xylenes/benzene ratio (~ 10 – 14) compared to the H-Z catalyst (~ 2 – 4.5). This can be explained on the basis of differences in pore size between the two zeolites. The H-M, because of its large pore size, allows bulky reactants to freely diffuse and react within its pores thereby giving more xylenes product. In the case of H-Z, some of the large molecules are restricted to react on the catalyst surface only.

4. Kinetic Modeling

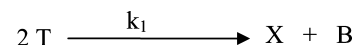
One of the main objectives of this study was to develop a comprehensive kinetic model which describes the transformation of 1,2,4-TMB in the presence of toluene over H-M and H-Z catalysts. Reaction schemes are hereby proposed on the basis of experimental product distribution. Three kinetic models have been developed based on the proposed reaction schemes.

4.1. Model Development. The following basic assumptions were made in deriving the model equations: (1) On the basis of

the assumption that isomerization and disproportionation proceed via a monomolecular and bimolecular mechanism, respectively, the isomerization reaction was described by a first order rate equation and the disproportionation by a second order rate equation. Similar assumptions were used by others in related studies.^{5,24} (2) An irreversible reaction path is assumed for both the transalkylation and disproportionation reactions. On the other hand, the isomerization reaction is assumed to proceed via a reversible path. (3) A single deactivation function is defined for all the reactions taking place.

4.1.1. Model I: Reaction of Toluene. The main reaction is the disproportionation of toluene (T) to give xylenes (X) and benzene (B) (Scheme 1).

Scheme 1



The following first order differential equations represent the model equations that were derived based on the above scheme. The rate of disappearance of toluene is

$$\frac{dy_T}{dt} = -2k_1 y_T^2 \frac{W_c W_{hc}}{V^2 MW_T} \varphi_1 \quad (1)$$

Rate of formation of xylenes:

$$\frac{dy_X}{dt} = k_1 y_T^2 \left(\frac{W_c W_{hc} MW_X}{V^2 MW_T^2} \right) \varphi_1 \quad (2)$$

where y_X is the mass fraction of species x in the riser simulator, MW_i is the molecular weight of species i in the system, V is the volume of the riser (45 cm³), W_{hc} is the weight of feed injected into the reactor (0.162 g), W_c is the mass of the catalyst (0.81 g of catalyst), and t is the time (seconds). The rate constant for the reaction was denoted by k_1 .

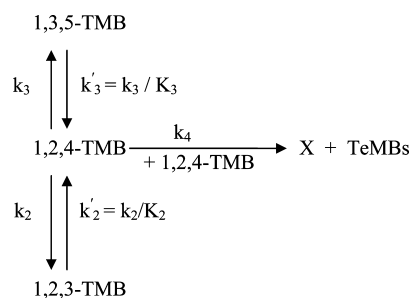
The temperature dependence of the rate constant was represented with the centered temperature form of the Arrhenius equation, i.e.,

$$k_1 = k_{o1} \exp \left[\frac{-E_i}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right) \right] \quad (3)$$

where T_o is an average temperature introduced to reduce parameter interaction, k_{o1} is the rate constant for the reaction at T_o , and E_i is the activation energy for the reaction. The time on stream (TOS) model was used to express the extent of catalyst deactivation during the reaction (i.e., $\varphi_1 = \exp(-\alpha_1 t)$), where α_1 is the deactivation constant (1/s) and t is time (s).

4.1.2. Model II: Reaction of 1,2,4-TMB. As shown in Scheme 2, the reactions involved are (i) isomerization of 1,2,4-TMB to 1,2,3-TMB, (i) isomerization of 1,2,4-TMB to 1,3,5-TMB, and (ii) disproportionation of 1,2,4-TMB to give TeMBs

Scheme 2



and xylenes (X). Minor reactions were not included in the model, like transalkylation of xylenes and TeMBs to give toluene and pentamethylbenzene (PeMB).

The following first order differential equations are the model equations that were derived based in Scheme 2. The rate of disappearance of 1,2,4-TMB

$$\frac{dy_{124\text{TMB}}}{dt} = -\left\{k_2\left(y_{124\text{TMB}} - \frac{y_{123\text{TMB}}}{K_2}\right)\frac{W_c}{V} + k_3\left(y_{124\text{TMB}} - \frac{y_{135\text{TMB}}}{K_3}\right)\frac{W_c}{V} + 2k_4y_{124\text{TMB}}^2\left(\frac{W_c W_{hc}}{V^2 MW_{124\text{TMB}}}\right)\right\}\varphi_2 \quad (4)$$

Rate of formation of xylenes

$$\frac{dy_X}{dt} = k_4y_{124\text{TMB}}^2\left(\frac{W_c W_{hc} MW_X}{V^2 MW_{124\text{TMB}}^2}\right)\varphi_2 \quad (5)$$

Rate of formation of 1,2,3-TMB

$$\frac{dy_{123\text{TMB}}}{dt} = k_2\left(y_{124\text{TMB}} - \frac{y_{123\text{TMB}}}{K_2}\right)\frac{W_c}{V}\varphi_2 \quad (6)$$

Rate of disappearance of 1,3,5-TMB

$$\frac{dy_{135\text{TMB}}}{dt} = k_3\left(y_{124\text{TMB}} - \frac{y_{135\text{TMB}}}{K_3}\right)\frac{W_c}{V}\varphi_2 \quad (7)$$

Rate constants for the reactions were denoted by k_2 , k_3 , and k_4 . To reduce parameter interaction, the rate constants were reparameterized at a reference temperature T_0 in accordance with eq 3. The reference temperature chosen in this study is the average of the experimental temperatures studied, i.e., 350 °C.

The following definitions of equilibrium constants were used in order to ensure thermodynamic consistency between the forward and reverse reactions:

$$K_2 = \frac{k_2}{k_2'} = \left(\frac{c_{1,2,3\text{-TMB}}}{c_{1,2,4\text{-TMB}}}\right)_{\text{eq}} \quad (8)$$

$$K_3 = \frac{k_3}{k_3'} = \left(\frac{c_{1,3,5\text{-TMB}}}{c_{1,2,4\text{-TMB}}}\right)_{\text{eq}} \quad (9)$$

The equilibrium constants are independent of pressure and concentration but depend upon temperature. The temperature dependency of the equilibrium constant for each of the reversible reactions can be obtained by utilizing the following thermodynamic relation:

$$\ln K = -\frac{\Delta G_r^\circ}{RT} \quad (10)$$

where ΔG_r° is the standard molar Gibbs free energy of reaction, R is the universal gas constant, and T is temperature in Kelvin. By definition, ΔG_r° is the difference between the total Gibbs free energy of formation of products and the reactants at a chosen standard state. For a given product or reactant species i , the Gibbs free energy of formation of ideal gas at a temperature (T , K) can be calculated from the following correlation.²⁵

$$\Delta G_{f,i}^\circ = a_i + b_i T + c_i T^2 \quad (11)$$

where a_i , b_i , and c_i are correlation constants that are determined from the least-squares fits of data.

Table 3 presents the correlation coefficients for chemical substances that are of interest to this study. These values were

Table 3. Correlation Coefficients of Gibbs Free Energy of Formation of Ideal Gas at a Temperature T^{25}

compound	a	b	c	T_{\min} (K)	T_{\max} (K)
1,2,4-TMB	-16.358	4.3119×10^{-1}	4.8564×10^{-5}	298.15	1000
1,3,5-TMB	-18.895	4.4166×10^{-1}	4.9679×10^{-5}	298.15	1000
1,2,3-TMB	-11.858	4.4140×10^{-1}	4.9389×10^{-5}	298.15	1000

taken from a comprehensive list prepared by Yaws and Chiang.²⁵ It should be noted that the standard state chosen for the calculation of ΔG_r° based on eq 11 was that of an ideal gas at temperature of 25 °C. With the utilization of the coefficients given in Table 3, the temperature dependency of the equilibrium constants for the two reversible reactions shown in Scheme 2 can be written as follows:

$$K_2 = \exp\left\{-\frac{541.26}{T} - 1.228 - 9.923 \times 10^{-5}T\right\} \quad (12)$$

$$K_3 = \exp\left\{\frac{269.06}{T} - 1.2593 - 1.3411 \times 10^{-4}T\right\} \quad (13)$$

where T is the temperature in Kelvin.

c_{TMB} is defined as the total molar concentration of the TMBs, i.e.,

$$c_{\text{TMB}} = c_{1,2,4\text{-TMB}} + c_{1,2,3\text{-TMB}} + c_{1,3,5\text{-TMB}} \quad (14)$$

The combination of eqs 8, 9, and 14 leads to the following expressions for the equilibrium concentration of the individual TMB isomers:

$$\left(\frac{c_{1,2,4\text{-TMB}}}{c_{\text{TMB}}}\right)_{\text{eq}} = \frac{1}{1 + K_2 + K_3} \quad (15)$$

$$\left(\frac{c_{1,2,3\text{-TMB}}}{c_{\text{TMB}}}\right)_{\text{eq}} = \frac{K_2}{1 + K_2 + K_3} \quad (16)$$

$$\left(\frac{c_{1,3,5\text{-TMB}}}{c_{\text{TMB}}}\right)_{\text{eq}} = \frac{K_3}{1 + K_2 + K_3} \quad (17)$$

Figure 6 displays equilibrium concentrations of 1,2,4-TMB, 1,2,3-TMB, and 1,3,5-TMB as a function of temperature. Equations 13–15 together with equilibrium constants given by eqs 10 and 11 were used in generating this figure. Also shown

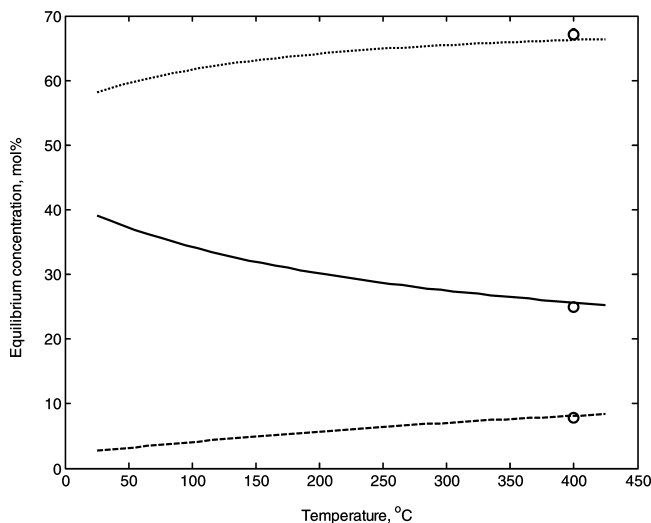
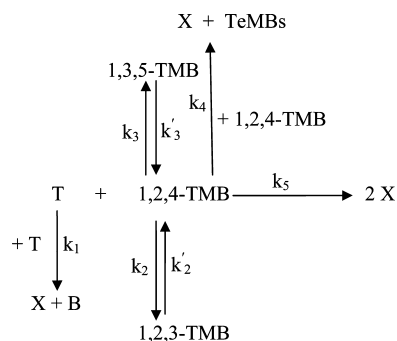


Figure 6. Equilibrium concentrations of isomers of TMB as a function of temperature: ---, 1,2,3-TMB; ···, 1,2,4-TMB; —, 1,3,5-TMB. The circles represent literature values reported in ref 23.

Scheme 3



in the figure are literature values, as reported by Norval and Phillips,²³ of the equilibrium distribution of the TMB isomers at 400 °C. It can be seen that the results obtained from the correlations closely match the reported literature values. The figure indicates that the formation of 1,3,5-TMB is thermodynamically favored at low temperatures while the formation of the other two isomers is more favorable at high temperatures.

4.1.3. Model III: Reaction of 1,2,4-TMB and Toluene.

Scheme 3 shows the proposed reactions taking place in this case. It can be seen that the reactions involved are (i) disproportionation of toluene to give xylenes (X) and benzenes, (ii) isomerization of 1,2,4-TMB to 1,2,3-TMB, (iii) isomerization of 1,2,4-TMB to 1,3,5-TMB, (iv) disproportionation of 1,2,4-TMB to give TeMBs and xylenes (X), and (v) transalkylation of 1,2,4-TMB with toluene to give xylenes.

Model equations derived from Scheme 3 are given as follows. The rate of disappearance of toluene

$$\frac{dy_T}{dt} = - \left\{ 2k_1 y_T^2 \left(\frac{W_c W_{hc}}{V^2 M W_T} \right) + k_5 y_T y_{124TMB} \left(\frac{W_c W_{hc}}{V^2 M W_{124TMB}} \right) \right\} \varphi_3 \quad (18)$$

Rate of disappearance of 1,2,4-TMB

$$\begin{aligned} \frac{dy_{124TMB}}{dt} = & - \left\{ k_2 \left(y_{124TMB} - \frac{y_{123TMB}}{K_2} \right) \frac{W_c}{V} + \right. \\ & k_3 \left(y_{124TMB} - \frac{y_{135TMB}}{K_3} \right) \frac{W_c}{V} + 2k_4 y_{124TMB}^2 \left(\frac{W_c W_{hc}}{V^2 M W_{124TMB}} \right) + \\ & \left. k_5 y_T y_{124TMB} \left(\frac{W_c W_{hc}}{V^2 M W_T} \right) \right\} \varphi_3 \quad (19) \end{aligned}$$

Rate of formation of xylenes:

$$\begin{aligned} \frac{dy_X}{dt} = & \left\{ k_1 y_T^2 \left(\frac{W_c W_{hc} M W_X}{V^2 M W_T^2} \right) + k_4 y_{124TMB}^2 \left(\frac{W_c W_{hc} M W_X}{V^2 M W_{124TMB}^2} \right) + \right. \\ & \left. 2k_5 y_T y_{124TMB} \left(\frac{W_c W_{hc} M W_X}{V^2 M W_T M W_{124TMB}} \right) \right\} \varphi_3 \quad (20) \end{aligned}$$

Rate of formation of 1,2,3-TMB:

$$\frac{dy_{123TMB}}{dt} = k_2 \left(y_{124TMB} - \frac{y_{123TMB}}{K_2} \right) \frac{W_c}{V} \varphi_3 \quad (21)$$

Rate of disappearance of 1,3,5-TMB:

$$\frac{dy_{135TMB}}{dt} = k_3 \left(y_{124TMB} - \frac{y_{135TMB}}{K_3} \right) \frac{W_c}{V} \varphi_3 \quad (22)$$

Table 4. Kinetic Parameters for Toluene Transformation over H-Mordenite and H-ZSM-5

	$k_1 \times 10^5$ (m ⁶ /(kg cat. s))	E_1 (kJ/mol)	α_1
H-Mordenite (H-M)			
values	1.01	54.22	0.06
95% CL	0.14	4.35	0.02
H-ZSM-5 (H-Z)			
values	1.47	41.61	0.11
95% CL	0.10	1.94	0.01

The symbols used in this section have similar meanings to the ones given in previous sections.

4.2. Determination of Model Parameters. There are 3 parameters in model I (k_{o1} , E_1 , and α_1), 7 parameters in model II (k_{o2} , k_{o3} , k_{o4} , E_2 , E_3 , E_4 , and α_2) and 11 parameters in model III (k_{o1} , k_{o2} , k_{o3} , k_{o4} , k_{o5} , E_1 , E_2 , E_3 , E_4 , E_5 , and α_3). A nonlinear regression method that employs the Gauss–Newton algorithm with Levenberg–Marquardt²⁶ modifications for global convergence was used to find the optimum parameters that minimize the sum of squares of the deviations between the calculated and experimental values of the mass fractions of reaction components, i.e.,

$$\text{OF} = \sum_{j=1}^n (y_j^{\text{exp}} - y_j^{\text{cal}})^2 \quad (23)$$

where OF is the objective function that was minimized and n is the number of experimental data points. The y_j^{cal} are evaluated by solving the model equations [eqs 1 and 2 for model I, eqs 4–7 for model II, and eqs 18–22 for model III] numerically using an explicit fourth-order Runge–Kutta ODE solver which is available in the MATLAB package. It can be noticed that the parameters of models I and II are a subset of the parameters belonging to the comprehensive model (i.e., model III). It was therefore decided to fit models I and II first and then use the estimated values from these models in model III. This strategy was adopted in order to reduce correlation between kinetic parameters in the comprehensive model.

4.2.1. Parameters for Model I. The values of the optimized kinetic parameters for model I (toluene reaction) along with their corresponding 95% confidence limits (CLs) are shown in Table 4 for reactions over the H-M and H-Z catalysts. It can be observed from the tabulated results that the apparent activation energy for the disproportionation of toluene over H-M was 54.22 ± 4.35 kJ/mol, while a slightly lower value of 41.61 ± 1.94 kJ/mol was obtained over the H-Z catalyst. Bhavikatti and Patwardhan²⁷ reported a value of 60.7 kJ/mol for the activation energy of toluene disproportionation over the Ni/mordenite. Chang et al.²⁸ obtained a value of 54.3 kJ/mol for the same reaction over a commercial solid catalyst. It can be seen that the values obtained in the present study are similar in magnitude to values reported in the literature.^{27,28} It is important to note that model predictions as presented in parts a and b of Figure 7 show a higher toluene conversion with H-M, which is in agreement with experimental results, even though the value of activation energy over H-M was slightly higher than the one over H-Z. This is because it is not only activation energy that dictates the value of conversion. The other kinetic parameters (i.e., a pre-exponential factor and deactivation constant) also play a significant role in determining the value of conversion.

Table 5 presents correlation matrices for model I over H-M and H-Z catalysts. For a model containing n parameters, the correlation matrix represents a square matrix ($n \times n$) that shows the correlation between all binary pairs of the parameters used

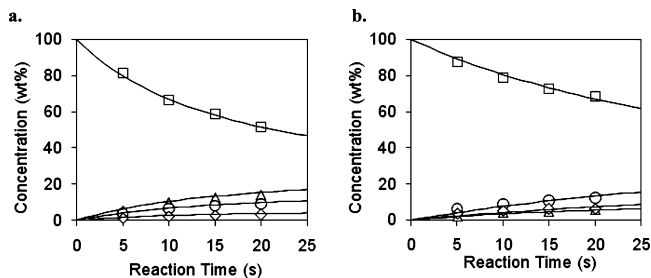


Figure 7. Comparison between experimental results and numerical simulations for reaction of 1,2,4-TMB on (a) H-M and (b) H-Z at reaction temperature of 400 °C. □, 1,2,4-TMB; ○, total xylenes; ◇, 1,3,5-TMB; Δ, 1,2,3-TMB.

Table 5. Correlation matrix for H-mordenite and H-ZSM-5 (Toluene transformation)

	k_1	E_1	α_1
H-Mordenite (H-M)			
k_1	1	-0.3268	0.9232
E_1	-0.3268	1	-0.0543
α_1	0.9232	-0.0543	1
H-ZSM-5 (H-Z)			
k_1	1	-0.1968	0.9518
E_1	0.1968	1	-0.0343
α_1	-0.9518	-0.0343	1

in the model. The value of each element of the matrix varies between -1 and +1. Values close to either -1 or +1 indicate a strong correlation while values close to zero signify the absence of correlation between the given pair of parameters. For a good parameter set, the correlation between any given pair should be very low, i.e., close to zero. A cross-correlation above ~0.98 or below ~-0.98 indicate that the parameters are highly correlated.²⁹ It can be observed that there is weak correlation between the pre-exponential factor and activation energy as well as between the activation energy and deactivation constant. However, there is some degree of correlation between the pre-exponential factor and deactivation constant which proves to be difficult to break.

4.2.2. Parameters for Model II. Table 6 shows regressed values of parameters for model II (TMB reaction) and their 95% CLs over H-M and H-Z catalysts. The values of apparent activation energies reported in Table 6 shows that on the H-M catalyst the isomerization of 1,2,4-TMB to 1,3,5-TMB ($E_3 = 7.92$ kJ/mol) is easier than the isomerization of 1,2,4-TMB to 1,2,3-TMB ($E_2 = 13.12$). In contrast, on the H-Z catalyst the apparent activation for the 1,2,4-TMB to 1,3,5-TMB isomerization ($E_3 = 45.93$ kJ/mol) is higher than that of the 1,2,4-TMB to 1,2,3-TMB isomerization ($E_2 = 32.73$ kJ/mol). It is also clear by comparing corresponding values of E_1 , E_2 , and E_3 that the transformation of the 1,2,4-TMB is easier over H-M as compared to H-Z. This can be attributed to an increased rate of bimolecular reaction over H-M. The large pore size of H-M allows it to accommodate higher concentrations of bulky TMB molecules inside its channel system.

As shown in Table 6, the apparent activation energy for the disproportionation reaction of 1,2,4-TMB was found to be 12.22 kJ/mol over the H-M catalyst while in the case of the H-Z catalyst the estimated value was 38.14 kJ/mol. Thus, the apparent activation energy over H-Z is more than 3 times of the value over the H-M catalyst. Atias et al.²⁴ have reported activation energies for the disproportionation of 1,2,4-TMB over two HY zeolites with different crystal sizes. The values of activation energies reported in their study (6.7 and 7.5 kJ/mol) are close to our result for the H-M catalyst. Furthermore, in a

similar study by Al-Khattaf et al.,⁵ an apparent activation energy of 7.1 kJ/mol was reported for 1,2,4-TMB disproportionation over the USY zeolite.

The values of the correlation coefficients for H-M and H-Z catalysts are displayed in Table 7. The cross-correlation matrix gives good results as indicated by the low correlation between most of the parameters. The only exception is the case between k_2 and α_2 where some level of interaction is observed.

4.2.3. Parameters for Model III. The kinetic parameters k_{01} to k_{04} and E_1 to E_4 in model III (TMB and toluene reaction) were fixed using regressed values obtained from models I and II. The remaining three parameters (i.e. k_{05} , E_5 , and α_3) were fitted to model III using experimental data of the transformation of an equimolar feed of toluene and 1,2,4-TMB. Values of kinetic parameters and their associated 95% confidence limits as obtained from the regression analysis are presented in Table 8 for H-M and H-Z catalysts. Low values of confidence limits point to the statistical significance of the regressed model parameters. This is further reinforced by the lack of significant cross-correlation between most of the parameters as can be seen in the correlation matrices presented in Table 9.

The apparent activation energy for the transalkylation of 1,2,4-TMB with toluene was found to be 7.21 kJ/mol over the H-M catalyst, while the value over the H-Z catalyst was 63.54 kJ/mol. A value of 21.56 kJ/mol was reported by Al-Khattaf et al.³⁰ in their study of a similar reaction over the USY catalyst. Graphical comparisons between the experimental and model predictions based on the optimized parameters for models I, II, and III are shown in Figures 7–9. For the sake of brevity, the plots are presented at one temperature only (i.e., 400 °C). It can be seen that there is an accurate match between the experimental values and the model predictions. It must be pointed out that the quality of the fits for the other two temperatures (300 and 350 °C), which were not shown here, is similar to the ones displayed in Figures 7–9.

4.3. Discussion of Kinetic Modeling Results. Table 8 shows a significant difference between the values of the apparent activation energy of 1,2,4-TMB over H-M and H-Z. This can be attributed to differences in pore size between the two catalysts. While H-Z is a medium-pore zeolite containing two types of intersecting channels, near-circular (0.54–0.56 nm) zigzag channels and elliptical (0.51–0.55) straight-chain channels,³¹ H-M is a one-dimensional large-pore zeolite with a nominal free diameter of 0.67–0.70 nm.²¹ The pore structure significantly influences the activity and selectivity of reactions in zeolites. As shown by Levenspiel,³² the apparent activation energy under strong diffusional resistance is one-half of the true activation energy, i.e.,

$$E_{app} = \frac{E_{int} + E_D}{2} \quad (24)$$

where E_{int} and E_D stand for intrinsic and diffusion activation energies, respectively. The 1,2,4-TMB (critical diameter of 0.76 nm) is expected to encounter considerable diffusional resistance over H-Z (pore size of ~0.6 nm).²² On the other hand, the large pore size of H-M (0.7 nm) would allow the 1,2,4-TMB molecule to pass without much hindrance even though the channel diameter of the zeolite is smaller than the critical size of the 1,2,4-TMB molecule. It is important to note that molecules are not rigid bodies and neither are the zeolites. Both molecules and windows vibrate, and mutual distortion of the two occur when molecules penetrate through the zeolite framework.²¹

The difficulties experienced by a molecule when passing through the channels of zeolites depend on the geometry and

Table 6. Kinetic Parameters for 1,2,4-TMB Transformation over H-Mordenite and H-ZSM-5

	$k_{2,0} \times 10^5$ (m ³ /(kg cat. s))	E_2 (kJ/mol)	$k_{3,0} \times 10^5$ (m ³ /(kg cat. s))	E_3 (kJ/mol)	$k_4 \times 10^5$ (m ⁶ /(kg cat. s))	E_4 (kJ/mol)	α_2
H-Mordenite (H-M)							
values	20.397	13.12	50.481	7.92	2.844	12.22	0.010
95% CL	1.542	2.03	1.356	2.12	0.033	0.94	0.002
ZSM-5 (H-Z)							
values	17.069	32.73	25.678	45.93	0.541	38.14	0.010
95% CL	1.405	6.58	1.540	4.69	0.040	5.84	0.002

Table 7. Correlation Matrix for H-Mordenite and H-ZSM-5 (1,2,4-TMB Transformation)

	k_2	E_2	k_3	E_3	k_4	E_4	α_2
H-Mordenite (H-M)							
k_2	1	-0.0947	-0.12	0.0066	-0.351	0.0553	0.7367
E_2	-0.0947	1	0.0065	-0.121	0.0553	-0.3535	-0.0947
k_3	-0.12	0.0065	1	0.0234	-0.3305	0.0339	-0.12
E_3	0.0066	-0.121	0.0234	1	0.0342	-0.334	0.0066
k_4	-0.351	0.0553	-0.3305	0.0342	1	-0.0967	-0.351
E_4	0.0553	-0.3535	0.0339	-0.334	-0.0967	1	0.0553
α_2	0.7367	-0.0947	-0.12	0.0066	-0.351	0.0553	1
H-ZSM-5 (H-Z)							
k_2	1	-0.5727	-0.1305	0.0894	-0.4599	0.2786	0.8842
E_2	-0.5727	1	0.0867	-0.1272	0.2786	-0.4598	-0.5727
k_3	-0.1305	0.0867	1	-0.7401	-0.4501	0.307	-0.1305
E_3	0.0894	-0.1272	-0.7401	1	0.3164	-0.4403	0.0894
k_4	-0.4599	0.2786	-0.4501	0.3164	1	-0.5866	-0.4599
E_4	0.2786	-0.4598	0.307	-0.4403	-0.5866	1	0.2786
α_2	0.8842	-0.5727	-0.1305	0.0894	-0.4599	0.2786	1

Table 8. Kinetic Parameters for Transalkylation of 1,2,4-TMB with Toluene over H-Mordenite and H-ZSM-5

	$k_5 \times 10^5$ (m ⁶ /(kg cat. s))	E_5 (kJ/mol)	α_3
H-Mordenite (H-M)			
values	0.551	7.21	0.010
95% CL	0.032	2.06	0.005
ZSM-5 (H-Z)			
values	0.792	63.54	0.010
95% CL	0.280	2.04	0.001

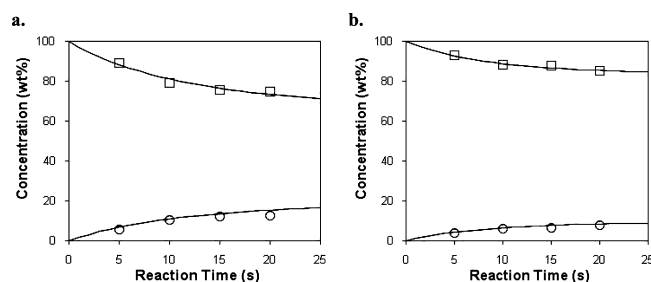
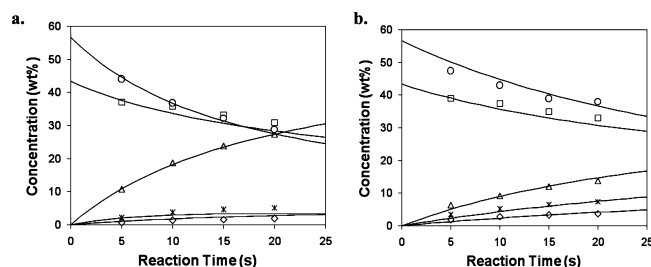
Table 9. Correlation Matrix for H-Mordenite and H-ZSM-5 (Toluene and 1,2,4-TMB Transalkylation Reaction)

	k_5	E_5	α_3
H-Mordenite (H-M)			
k_5	1	0.0857	0.8958
E_5	0.0857	1	0.0687
α_3	0.8958	0.0687	1
H-ZSM-5 (H-Z)			
k_5	1	-0.7383	0.6847
E_5	-0.7383	1	-0.2300
α_3	0.6847	-0.2300	1

the precise interaction between the sorbate and the zeolite. Molecules with a favorable configuration and compressibility can squeeze themselves and diffuse through channels with a diameter less than their critical molecular size.³³ The relative ease of diffusion of 1,2,4-TMB over H-M means that the magnitude of the diffusion activation energy of the molecule over H-Z would be higher than that over H-M. In other words, $E_{D,(H-ZSM-5)} > E_{D,(H-M)}$. It can, therefore, be inferred from eq 24 that the difference in diffusion activation energy is what is responsible for the difference in the apparent activation energy of 1,2,4-TMB over the two zeolites.

In contrast to 1,2,4-TMB reaction and the transalkylation reaction, the apparent activation energy of toluene over H-M is higher than that over H-Z. Toluene, which has a molecular critical diameter of 0.67 nm, can diffuse through H-Z without

encountering great diffusional constraint. This is evident from effectiveness factor value of greater than 0.95 that was reported by Sotelo et al.³² in their study of toluene alkylation over ZSM-5. In addition, literature results of the diffusion coefficients of toluene in the two zeolites points that the diffusion of toluene is easier in H-M compared to H-Z. For instance, Roheque-Malherbe et al.³⁴ reported the diffusivity of toluene at 127 °C over H-Z to be 6×10^{-9} cm²/s while Beecher et al.³⁵ found the diffusivity of the same molecule to be about 200 times larger over the H-M catalyst at 93.3 °C. It is thus clear that diffusional

**Figure 8.** Comparison between experimental results and numerical simulations for reaction of toluene on (a) H-M and (b) H-Z at a reaction temperature of 400 °C: □, toluene; ○, total xylenes.**Figure 9.** Comparison between experimental results and numerical simulations for reaction of 1,2,4-TMB and toluene on (a) H-M and (b) H-Z at reaction temperature of 400 °C: □, toluene; ◇, 1,2,4-TMB; ○, total xylenes; *, 1,3,5-TMB; △, 1,2,3-TMB.

limitation is not likely to be the main contributing factor in explaining the difference between the apparent activation energies over the two catalysts. It is known that the intrinsic activation energy is a function of catalyst acidity. High acidity of the catalyst leads to low intrinsic activation energy. Since H-Z is 3.3 times more acidic than H-M, as shown in Table 1, it is logical to assume that the intrinsic activation energy of toluene is higher over H-M. This, in conjunction with eq 24, consequently points to the reason why the apparent activation energy of toluene over H-M is higher than that over the H-Z catalyst.

5. Conclusions

This paper has presented the results of experimental and modeling study on the catalytic transformation of toluene, 1,2,4-TMB, and an equimolar mixture of toluene and 1,2,4-TMB over H-mordenite and H-ZSM-5 catalysts. The conclusions of this study are the following: (1) H-mordenite was found to give a higher level of conversion of toluene and 1,2,4-TMB when compared to H-ZSM-5. This is attributed to the larger pore structure of H-mordenite. (2) The feed 1,2,4-TMB was more reactive than toluene over the two catalysts which is in agreement with what was reported in related studies. (3) Several advantages were found in the transalkylation of 1,2,4-TMB with toluene over the transformation of either toluene or 1,2,4-TMB. These include, among others; higher total conversion of toluene and 1,2,4-TMB, higher xylenes/TMB isomers ratio, and higher amount of total xylenes. (4) A comprehensive kinetic model that accounts for reversibility of the isomerization reaction based on values of temperature-dependent thermodynamic equilibrium constants was developed. The parameters of the developed model were estimated using the nonlinear regression technique. The models were found to give a good match of experimental data based on a statistically significant estimate of the kinetic parameters in the models. For the 1,2,4-TMB reaction and transalkylation of 1,2,4-TMB with toluene, the apparent activation energy over H-Z was higher than that over H-M (i.e., $E_{app,(H-Z)} > E_{app,(H-M)}$). The reverse order was observed for the toluene reaction over the two catalysts. (5) A simple correlation that gives an accurate representation of the temperature dependency of thermodynamic equilibrium compositions of TMBs isomers was reported.

Acknowledgment

The authors express their appreciation to the support from the Ministry of Higher Education, Saudi Arabia, in establishment of the Center of Research Excellence in Petroleum Refining & Petrochemicals at King Fahd University of Petroleum & Minerals (KFUPM). Acknowledgement is also due to Mr Mariano Gica for assistance in experimental tests.

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)
 G = Gibbs free energy (kJ/mol)
 k = apparent kinetic rate constant (m³/(kg cat s))
 k_0 = apparent kinetic rate constant at average temperature T_0 [m³/(kg cat s)], units based on first order reaction
 K = equilibrium constant (dimensionless)
 MW_i = molecular weight of species i (kg/mol)
 R = universal gas constant (kJ/(mol K))
 t = reaction time (s)
 T = reaction temperature (K)

T_0 = average temperature of the experiment (K)

V = volume of the riser (45 cm³)

W_c = mass of the catalysts (0.81 g cat)

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

Y_i = mass fraction of the i th component (wt %)

Chemical Species

B = benzene

T = toluene

TeMBs = tetramethylbenzenes

TMBs = trimethylbenzenes

X = xylenes

Ratios

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

Greek Letter

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

Literature Cited

- Roldán, R.; Romero, F. J.; Jiménez, C.; Borau, V.; Marinas, J. M. Transformation of mixtures of benzene and xylenes into toluene by transalkylation on zeolites. *Appl. Catal., A* **2004**, *266*, 203–210.
- Čejka, J.; Wichterlova, B. Acid-catalyzed synthesis of mono- and dialkylbenzenes over zeolites: Active sites, zeolite topology, and reaction mechanisms. *Catal. Rev.* **2002**, *44*, 375–422.
- Tsai, T. C.; Liu, S. B.; Wang, I. Disproportionation and transalkylation of alkylbenzenes over zeolite catalysts. *Appl. Catal., A* **1999**, *181*, 355–398.
- Čejka, J.; Kotrla, J.; Krejčí, A. Disproportionation of trimethylbenzenes over large pore zeolites: catalytic and adsorption study. *Appl. Catal., A* **2004**, *277*, 191–199.
- Al-Khattaf, S.; Tukur, N. M.; Al-Amer, A.; Al-Mubaiyedh, U. Catalytic transformation of C₇–C₉ methyl benzenes over USY-based FCC zeolite catalyst. *Appl. Catal., A* **2006**, *305*, 21–31.
- Das, J.; Bhat, Y. S.; Bhardwaj, A. I.; Halgeri, A. B. Zeolite beta catalyzed C₇ and C₉ aromatics transformation. *Appl. Catal., A* **1994**, *116*, 71–79.
- Wang, I.; Tsai, T. C.; Huang, S. T. Disproportionation of toluene and of trimethylbenzene and their transalkylation over zeolite beta. *Ind. Eng. Chem. Res.* **1990**, *29*, 2005–2012.
- Röger, H. P.; Möller, K. P.; O'Connor, C. T. The Reaction Network in the Conversion of 1,2,4-Trimethylbenzene over HZSM-5. *J. Catal.* **1998**, *176*, 68–75.
- Čejka, J.; Krejčí, A.; Žilková, N.; Dědeček, J.; Hanika, J. Alkylation and disproportionation of aromatic hydrocarbons over mesoporous molecular sieves. *Microporous Mesoporous Mater.* **2001**, *44*, 499–507.
- Park, S. H.; Rhee, H. K. Shape selective conversion of 1, 2, 4-trimethylbenzene over zeolite NU-87. *Catal. Today* **2000**, *63*, 267–273.
- Dumitriu, E.; Guimon, C.; Hulea, V.; Lutic, D.; Fecete, I. Transalkylation of toluene with trimethylbenzenes catalyzed by various AFI catalysts. *Appl. Catal., A* **2002**, *237*, 211–221.
- Tsai, T. C.; Chen, W.; Lai, C.; Liu, S.; Wang, I.; Ku, C. S. Kinetics of toluene disproportionation over fresh and coked H-mordenite. *Catal. Today* **2004**, *97*, 297–302.
- Tsai, T. S. Reactivation of acidic sites in mordenite used in toluene disproportionation. *Appl. Catal., A* **2006**, *301*, 292–298.
- Wu, J. C.; Leu, L. J. Toluene disproportionation and transalkylation reaction over mordenite zeolite catalysts. *Appl. Catal.* **1983**, *7*, 283–294.
- Das, J.; Bhat, Y. S.; Halgeri, A. B. Transalkylation and disproportionation of toluene and C₉ aromatics over zeolite beta. *Catal. Lett.* **1994**, *23*, 161–168.
- Čejka, J.; Krejčí, A.; Hanika, J. The effect of zeolite structure on the disproportionation of trimethylbenzene to xylenes and tetramethylbenzenes. *Stud. Surf. Sci. Catal.* **1999**, *125*, 351–358.
- Chu, S.; Chen, Y. The conversions of 1,3,5-trimethylbenzene over beta zeolite: Effect of SiO₂/Al₂O₃ ratio. *Chem. Technol. Biotechnol.* **1998**, *72*, 1–6.
- Mikhail, S.; Ayoub, S. M.; Barakat, Y. Conversion of trimethylbenzenes over Y-zeolite catalyst. *Zeolites* **1987**, *7*, 231–234.
- de Lasa, H. I. Riser simulator for catalytic cracking studies. U.S. Patent 5,102,628, April 17, 1992.
- Kraemer, D. W. Ph.D. Dissertation, University of Western Ontario, London, Canada, 1991.

- (21) Karger, J.; Ruthven, D. M. *Diffusion in Zeolites and Other Microporous Solids*; Wiley: New York, 1992.
- (22) Olson, D. H.; Haag, W. O. Structure-selectivity relationship in xylene isomerization and selective toluene disproportionation. *Am. Chem. Soc. Symp. Ser.* **1984**, 248, 275.
- (23) Norval, G. W.; Phillips, M. J. Alkylation of toluene with ethylene: An equilibrium approach. *React. Kinet. Catal. Lett.* **1989**, 38, 261–264.
- (24) Atias, J. A.; Tonetto, G.; de Lasa, H. Catalytic conversion of 1,2,4-trimethylbenzene in a CREC riser simulator. A heterogeneous model with adsorption and reaction phenomena. *Ind. Eng. Chem. Res.* **2003**, 42, 4162–4173.
- (25) Yaws, C. L.; Chiang, P. Y. Enthalpy of formation for 700 major organic compounds. *Chem. Eng.* **1988**, 95, 81–88.
- (26) Marquardt, D. An algorithm for least-squares estimation of nonlinear inequalities. *SIAM J. Appl. Math.* **1963**, 11, 431–441.
- (27) Bhavikatti, S. S.; Patwardhan, S. R. Toluene disproportionation over nickel-loaded aluminum-deficient mordenite. 2. Kinetics. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, 20, 106–109.
- (28) Chang, J. R.; Sheu, F. C.; Cheng, Y. M.; Wu, J. C. Kinetics and optimization of the toluene disproportionation reaction over solid acid catalysts. *Appl. Catal.* **1987**, 33, 39–53.
- (29) Johnson, M. L., Parameter correlations while curve fitting. In *Numerical Computer Methods*, Part C, Vol. 321, Methods in Enzymology Series; Johnson, M. L., Brand, L., Eds.; Academic Press: San Diego, CA, 2000; pp 426–446.
- (30) Al-Khattaf, S.; Tukur, N. M.; Al-Amer, A. 1,2,4-Trimethylbenzene transformation reaction compared with its transalkylation reaction with toluene over USY zeolite catalyst. *Ind. Eng. Chem. Res.* **2007**, 46, 4459–4467.
- (31) Kokotailo, G. T.; Lowten, S. L.; Olson, D. H.; Meir, W. M. Structure of synthetic zeolite ZSM-5. *Nature* **1978**, 272, 437.
- (32) Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; John Wiley & Sons: New York, 1999.
- (33) Sotelo, J. L.; Uguina, M. A.; Valverde, J. L.; Serrano, D. P. Kinetics of toluene alkylation with methanol over Mg-modified ZSM-5. *Ind. Eng. Chem. Res.* **1993**, 32, 2548–2554.
- (34) Roque-Malherbe, R.; Wendelbo, R.; Mifsud, A.; Corma, A. Diffusion of aromatic hydrocarbons in H-ZSM-5, H-Beta and H-MCM-22 zeolites. *J. Phys. Chem.* **1995**, 99, 14064–14071.
- (35) Beecher, R.; Voorhies, A.; Eberley, P. Hydrocracking and diffusion of pure compounds on mordenite catalysts. *Ind. Eng. Chem. Prod. Res. Dev.* **1968**, 7, 203–209.

Received for review March 8, 2010

Revised manuscript received May 6, 2010

Accepted June 8, 2010

IE100527X