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# Catalytic Transformation of Toluene over a High-Acidity Y-Zeolite Based Catalyst

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The catalytic transformation of toluene has been investigated over Y-zeolite-based catalysts in a novel riser simulator under different operating conditions. Several experiments were performed in the temperature range of 400–500 °C to understand the transformation of toluene over a high-acidity Y-based zeolite catalyst (H-Y). It has been observed that toluene can transform either through disproportionation, producing benzene and xylene isomers, or through dealkylation, producing gases and benzene. The rates of both reactions are essentially dependent on the reaction temperature. The dealkylation reaction was determined to be favored by high temperature. The benzene/xylene ratio was determined to increase with temperature, because of the high xylene dealkylation rate. Toluene transformation was determined to be controlled by both Y-zeolite acidity and reaction temperature. While high acidity and high reaction temperature favor toluene dealkylation, medium acidity and low reaction temperature favor toluene disproportionation. Pseudo-homogeneous first-order kinetics was used to model toluene conversion. Two different deactivation functions were included in this model, and the kinetic constants were calculated based on these two different functions.

## 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. One common method for xylene production is conversion of the lower-value toluene (C<sub>7</sub>) into xylenes. A huge amount of research has been devoted for this purpose. It is well-known that toluene undergoes several simultaneous chemical reactions, which include disproportionation, transalkylation, dealkylation, and coke formation.

Toluene transformation is well documented in the literature.<sup>1–6</sup> This transformation can occur through two major different techniques. The first is toluene hydrodealkylation, where toluene is converted to benzene in the presence of hydrogen. The other technique is disproportionation, where two toluene molecules react together to form benzene and xylene. Mobil disproportionation process (TDP-3) is among the most famous commercial processes for toluene disproportionation.<sup>7</sup> Most of the reported studies on toluene disproportionation have been conducted at relatively high pressure and in the presence of hydrogen using a fixed-bed reactor. ZSM-5 zeolites can be used in toluene disproportionation to enhance para-selectivity to >90%.<sup>4–6</sup>

Pacheco Filho et al.<sup>8</sup> performed toluene disproportionation over a commercial mordenite catalyst in the presence of hydrogen. The toluene conversion was observed to increase steadily as the temperature was increased but decreased with the increase in space velocity. The catalyst was impregnated with 8.5 wt % of phosphorus to enhance *p*-xylene selectivity. Peng et al.<sup>9</sup> studied toluene transformation over dealuminated MCM-22 zeolites. The activity of MCM-22 was determined to be comparable to that of mordenite and much higher than that of ZSM-5. The fraction of *p*-xylene in xylene isomers (para-selectivity) formed on MCM-22 was higher than its equilibrium value, and increased further by the dealumination, because of the elimination of the framework Al atoms predominantly on the external surface and inside the 10-MR channels. Kaeding et al.<sup>5</sup> were able to produce benzene and xylenes that were rich in the para isomer (70%–90%) over ZSM-5 zeolites that were modified with phosphorus, boron, or magnesium compounds. The increment of *p*-xylene selectivity is due to the reduction of the dimensions of pore openings and channels sufficiently to favor formation and outward diffusion of *p*-xylene, the isomer with the smallest minimum dimension. Kunieda et al.<sup>10</sup> studied more than 20 forms of the synthesized ZSM-5 to investigate the source of selectivity of *p*-xylene formation. They suggested that *p*-xylene selectivity could be correlated with not only the diffusion rate but also the external solid acidity. Zheng et al.<sup>11</sup> modified HZSM-5 with antimony oxide to enhance diffusional constraints and to remove the unselective Brønsted acid sites, which led to enhanced *p*-xylene selectivity.

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Auer and Hofmann<sup>12</sup> studied the pore structure and the acidic properties of pillared clays based on montmorillonite and hectorite intercalated with aluminum-, zirconium-, and chromium-hydroxy oligomers. They determined that the catalytic activity of the optimal chromium-pillared clay is between that of H-ZSM-5 and an H-Y-zeolite. Yang et al.<sup>13</sup> investigated toluene reactions on hybrid catalysts composed of physically mixed NiS/SiO<sub>2</sub> and USY zeolite. It was suggested that the hydrogen species supplied by hydrogen spillover at NiS sites and interparticle migration promoted toluene disproportionation. Davidova et al.<sup>14</sup> noted that nickel-zeolite catalysts in the reduced form are active for toluene dealkylation and, under certain conditions, for the disproportionation reaction.

Two typical transalkylation side reactions exist in toluene disproportionation: the first one is the reaction between toluene and the produced xylene, and the second one is the reaction between two produced xylenes. Xylene dealkylation is a very important secondary reaction, especially with a high-acidity catalyst.<sup>15</sup> The first two secondary reactions form trimethylbenzene (TMB) and the xylene dealkylation reaction forms gases. Thus, if TMB is observed in the product, this is a sign of secondary transalkylation reactions. The presence of gases is a strong sign for the dealkylation reaction.

The detailed mechanism of toluene disproportionation over a ZSM-5 zeolite was reported by Xiong et al.<sup>1</sup> Two different reaction pathways were proposed: a methyl transfer mechanism (the formation of a methoxy group on the zeolite surface) and the diphenyl methane mechanism. It was shown that toluene disproportionation does not require Brønsted acid sites with a high acid strength (present in H-ZSM-5 zeolite) to proceed, and the rate of the reaction is controlled by the concentration of acid sites, which is higher in Y-zeolite, compared to H-ZSM-5.<sup>1</sup> Meshram<sup>16</sup> identified two types of active sites in H-ZSM-5: one that promoted disproportionation and the other promoted the dealkylation of toluene. The latter sites were determined to be suppressed by the incorporation of modifiers.

In 2002, a study on toluene disproportionation over a modified ZSM-5 zeolite catalyst was conducted by Kareem et al.<sup>6</sup> In this study, toluene disproportionation to produce benzene and *p*-xylene has been performed using an ion-exchanged HZSM-5 catalyst in a down-flow continuous fixed-bed reactor. The results indicate an increased toluene conversion, as well as a higher percentage of *p*-xylene yield beyond the equilibrium predicted level on a nickel-exchanged catalyst. On the other hand, magnesium- and chromium-exchanged catalysts gave the lowest yields.

Regarding the kinetics of the toluene reaction, it is still debated whether this reaction follows first or second-order kinetics. Aniek et al.<sup>17</sup> reported a first-order reaction for toluene reaction over Cu/AlF<sub>3</sub>-Y zeolite. Beltrame et al.<sup>18</sup> reported a second-order reaction between two adsorbed toluene molecules over ZSM-5. However, a first-order kinetics reaction was proposed by Nayak and Rieckert<sup>19</sup> and Bhaskar and Do.<sup>20</sup> Dooley

et al.<sup>21</sup> used Y-zeolite that contained nickel for toluene disproportionation. Most of their reactions were adequately fitted by second-order kinetics. Hydrogen was used as the carrier gas in most of these papers, and low coke formation was observed; hence, no deactivation effect was considered in their modeling. Uguina et al.<sup>15</sup> performed the reaction over a ZSM-5 zeolite in the absence of hydrogen. Das et al.<sup>22</sup> conducted a kinetic study for toluene disproportionation over modified MFI aluminosilicate, using hydrogen as a carrier gas. Their data were best fit with an irreversible first-order kinetics. Their model does not consider catalyst deactivation. They attributed this to a feature of the ZSM-5 zeolite that does not allow coke formation and deposition, especially inside the channels of MFI. A reversible heterogeneous model was used to represent toluene disproportionation. Autor and Hofman<sup>12</sup> reported that the kinetics of toluene disproportionation catalyzed by the optimal chromium-pillared clay can be described by a pseudo-first-order expression. Recently, Tsai et al.<sup>23</sup> derived reversible second-order kinetics for toluene disproportionation over mordenite zeolite.

It is obvious that most of the previous studies have used hydrogen as a carrier gas and have assumed low coke formation (in the presence or absence of hydrogen). Hence, no deactivation factor was considered in toluene reactions. In a previous study,<sup>24</sup> the effect of Y-zeolite acidity on *m*-xylene conversion has been investigated. It was found, however, that Y-zeolite affected only the reaction selectivity and it did not alter the catalyst activity much. In the present study, it is the objective of the study to highlight the role of Y-zeolite acidity on toluene transformation. The Y-zeolites have been steamed under different conditions to change the acidity, and no metal was added to them. The reaction is conducted over a fluidized-bed reactor, over a Y-zeolite catalyst, and without any hydrogen at atmospheric pressure. The reaction occurs within a relatively short contact time (3–15 s) at different temperatures. During the toluene reaction, an appreciable amount of coke is deposited (up to 1.7 wt % coke was formed) over the surface of the catalyst, which leads to partial catalyst deactivation. Two pseudo-homogeneous models were used to fit toluene transformation. These models include two different deactivation functions to account for the effect of coke deposition on the intrinsic catalyst activity.

## 2. Experimental Procedure

**2.1. The Riser Simulator.** All the experimental runs were performed in the riser simulator. This reactor is a novel bench-scale apparatus, invented by de Lasa,<sup>25</sup> with an internal recycle unit to overcome the technical problems of the standard microactivity test (MAT), and it is fast becoming a valuable experimental tool for reaction evaluation involving model compounds,<sup>26,2726–27</sup> and also for testing and developing new fluidized catalytic cracking (FCC) in vacuum gas oil (VGO) cracking.<sup>2828</sup> The riser simulator consists of two outer shells: the lower section and the upper section, which allow the catalyst to be loaded or unloaded easily. The reactor was designed in such way that an annular space is created between the outer portion of the basket and the inner part of the reactor

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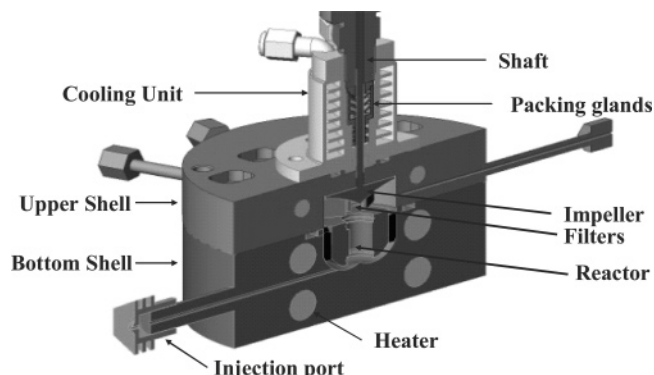


Figure 1. Schematic diagram of the riser simulator.

Table 1. Physicochemical Properties of the As-Prepared H-Y and Dealuminated Y-Zeolites

parameter	Value for Given Zeolite			
	H-Y	USY-1	USY-2	USY-3
steaming temperature (°C)		800	600	600
steaming time (h)		6	5	2
average crystal size (μm)	0.9	0.9	0.9	0.9
BET surface area (m <sup>2</sup> /g)	190	155	172	175
total acidity (mmol/g)	0.55	0.033	0.1	0.2

shell. A metallic gasket seals the two chambers with an impeller located in the upper section. A packing gland assembly and a cooling jacket that surrounds 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 the 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 the various riser simulator components, and the sequence of injection and sampling, can be found in the work by Kraemer.<sup>28</sup> A schematic diagram of the riser simulator is given in Figure 1.

**2.2. Materials.** Y-zeolite was obtained from the Tosoh Company. The Na-zeolite was ion-exchanged with  $\text{NH}_4\text{NO}_3$  to replace the  $\text{Na}^+$  cation with the ammonium ( $\text{NH}_4^+$ ) cation. Following this,  $\text{NH}_3$  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. The catalyst then was calcined for a period of 2 h at 600 °C. Next, the catalyst was calcined at 600 °C for 2 h. Finally, the fluidizable catalyst particles (with an average size of 60 μm) were treated with 100% steam at different temperatures and times to obtain the dealuminated Y (designated USY)-zeolites. The steaming conditions and the catalyst main properties are reported in Table 1. The surface area was measured using the Brunauer–Emmett–Teller (BET) method.

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

**2.3. Procedure.** Regarding the experimental procedure in the riser simulator, 0.8 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 ~250 °C and evacuated at ~0.5 psi to prevent any condensation of hydrocarbons inside the box. The heating of the riser simulator was conducted under a continuous flow of inert gases (argon), and the process usually takes a few hours until thermal equilibrium is finally attained. Meanwhile, before the initial experimental run, the catalyst was activated for 15 min at 620 °C in a stream of argon. The temperature controller was set to the desired reaction temperature, and, in the same manner, the timer was adjusted to the desired

Table 2. Toluene Conversions under Different Reaction Conditions

temperature/time	Toluene Conversion (%)			
	USY-1	USY-2	USY-3	H-Y
400 °C/5 s		3.6	5.7	9.3
400 °C/10 s	0.35	6.0	8.0	17.1
400 °C/15 s	0.75	8.8	13	23.3
450 °C/5 s		5.4	7.2	10.7
450 °C/10 s	0.52	12.0	14.3	19.6
450 °C/15 s	0.84	17.2	20.0	26.1
500 °C/5 s		5.5	6.7	11.2
500 °C/10 s	0.89	14.6	17.6	20.25
500 °C/15 s	1.65	22.1	24	27.1

reaction time. At this point, the gas chromatography (GC) apparatus is started and set to the desired conditions.

When the reactor and the gas chromatograph have reached the desired operating conditions, the feedstock was injected directly into the reactor, via a loaded syringe. After the reaction, the four-port valve immediately opens, ensuring that the reaction was terminated and the entire product stream was sent on-line to the analytical equipment via a preheated vacuum box chamber.

**2.4. 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 products were analyzed in an Agilent model 6890N gas chromatograph that was equipped with a flame ionization detection (FID) system and a capillary column (INNOWAX, 60 m cross-linked methyl silicone with an internal diameter of 0.32 mm).

Coke deposited on spent catalysts is 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 to carbon dioxide ( $\text{CO}_2$ ). The amount of coke formed is determined by measuring the number of moles of  $\text{CO}_2$ .

### 3. Results and Discussions

Catalytic experiments were performed in a riser simulator using different catalysts. Experiments were performed at a catalyst/toluene 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, many runs were repeated to check for reproducibility in the conversion results, which was determined to be excellent. Typical errors were in the range of ±2%.

**3.1. Catalyst Characterization.** The BET surface area was measured according to the standard procedure ASTM D-3663, using a Sorptomatic 1800 unit (Carlo Erba Strumentazione, Italy). The acid property of the catalyst was characterized by  $\text{NH}_3$  temperature-programmed desorption ( $\text{NH}_3$ -TPD). In all the experiments, 50 mg of sample were outgassed at 400 °C for 30 min in flowing helium and then cooled to 150 °C. At that temperature,  $\text{NH}_3$  was adsorbed on the sample by injecting pulses of 2 μL/pulse. The injection was repeated until the amount of  $\text{NH}_3$  detected was the same for the last two injections. After the adsorption of  $\text{NH}_3$  was saturated, the sample was flushed at 150 °C for 1 h with helium to remove excess  $\text{NH}_3$ , and then the temperature was programmed at 30 °C/min up to 1000 °C in flowing helium at 30 mL/min. FID equipment was used to monitor the desorbed  $\text{NH}_3$ . The results of the catalyst characterization are presented in Table 1.

**3.2. Conversion of Toluene.** A steamed sample of the used catalyst (USY-1) with a total acidity of 0.033 mmol/g and a surface area of 155 m<sup>2</sup>/g was used. As shown in Table 2, using this catalyst, no appreciable transformation of toluene was observed. Consequently, a nonsteamed catalyst (H-Y) with



Table 3. Product Distribution under Various Reaction Conditions for Toluene H-Y

temperature/time	conversion (%)	Product Distribution (wt %)										total xylene	total TMB
		gas	benzene	m-xylene	p-xylene	o-xylene	ethylbenzene	1,3,5-TMB <sup>a</sup>	1,2,4-TMB <sup>a</sup>	1,2,3-TMB <sup>a</sup>			
350 °C/3 s	1.6	0	0.1	0.3	0.14	0.12	0	0	0	0	0.6	0	
350 °C/5 s	4.3	0	2.6	0.8	0.4	0.4	0	0	0	0	1.6	0	
350 °C/7 s	7.6	0.1	4.3	1.5	0.7	0.6	0.07	0.1	0.15	0	2.9	0.25	
350 °C/10 s	12.63	0.2	6.8	2.6	1.2	1.1	0.17	.11	0.29	0	5.07	0.4	
350 °C/13 s	16.7	0.47	8.6	3.4	1.6	1.44	0.26	0.16	0.4	0.06	6.7	0.62	
350 °C/15 s	18.25	0.5	9.2	3.8	1.8	1.6	0.3	0.18	0.44	0.06	7.5	0.68	
400 °C/3 s	3.8	0.07	2.3	0.7	0.33	0.3	0	0	0.1	0	1.33	0.1	
400 °C/5 s	9.3	0.37	5.0	1.8	0.82	0.8	0.14	0.09	0.24	0	3.56	0.33	
400 °C/7 s	11.6	0.43	6.2	2.2	1.0	0.95	0.2	0.11	0.3	0.04	4.35	0.45	
400 °C/10 s	17.1	0.7	8.5	3.3	1.6	1.5	0.3	0.19	0.5	0.07	6.7	0.76	
400 °C/13 s	20.15	1.1	10.0	3.9	1.8	1.7	0.4	0.22	0.6	0.08	7.8	0.9	
400 °C/15 s	23.3	1.2	11.3	4.6	2.15	2.0	0.5	0.27	0.7	0.1	9.25	1.07	
450 °C/3 s	6.1	0.31	3.36	1.1	0.5	0.5	0.08	0.06	0.17	0	2.18	0.23	
450 °C/5 s	10.7	0.7	5.5	1.9	0.9	0.86	0.17	0.11	0.3	0.04	3.83	0.45	
450 °C/7 s	14.3	1.3	7.1	2.4	1.14	1.1	0.25	0.15	0.39	0.06	4.89	0.6	
450 °C/10 s	19.5	1.64	9.4	3.52	1.64	1.6	0.37	1.22	0.6	0.09	7.13	1.91	
450 °C/13 s	22	2.3	10.5	3.8	1.8	1.7	0.43	0.26	0.68	0.09	7.73	1.03	
450 °C/15 s	26.1	2.45	12.2	4.7	2.2	2.1	0.53	0.3	0.8	0.12	9.53	1.22	
500 °C/3 s	6.7	0.66	3.5	1.1	0.5	0.5	0.1	0.06	0.18	0	2.2	0.24	
500 °C/5 s	11.2	1.3	5.7	1.8	0.82	0.82	0.18	0.11	0.31	0.05	3.62	0.47	
500 °C/7 s	15.3	2	7.1	2.2	1.0	1.0	0.23	0.14	0.36	0.06	4.43	0.56	
500 °C/10 s	20.25	3	9.7	3.1	1.4	1.4	0.34	0.2	0.53	0.09	6.24	0.81	
500 °C/13 s	23.4	4	11.2	3.4	1.6	1.6	0.4	0.24	0.6	0.09	7	0.93	
500 °C/15 s	27.12	4.4	12.7	4.11	1.9	1.9	0.5	0.27	0.75	0.11	8.41	1.13	
550 °C/3 s	6.9	1.0	3.66	0.94	0.44	0.45	0.09	0.06	0.16	0	1.92	0.22	
550 °C/5 s	10.5	1.8	5.45	1.4	0.64	0.66	0.15	0.083	0.24	0	2.85	0.32	
550 °C/7 s	15.1	2.6	7.3	1.88	0.87	0.9	0.21	0.11	0.33	0.05	3.86	0.49	
550 °C/10 s	18.56	3.6	9.3	2.34	1.1	1.1	0.27	0.14	0.4	0.06	4.81	0.6	
550 °C/13 s	22.5	4.5	11.2	2.82	1.3	1.36	0.33	0.17	0.46	0.08	5.81	0.71	
550 °C/15 s	26.5	5.3	13.1	3.35	1.6	1.6	0.4	0.2	0.59	0.09	6.95	0.88	

higher acidity was used in this study. Mildly steamed catalysts (USY-2 and USY-3) were also used, for comparison purposes (section 3.3).

Using the current catalyst (H-Y) with high acidity has increased toluene reactivity, and better conversion was obtained than that of USY-1 catalyst with lower acidity. Table 3 shows that toluene conversion increases with both contact time and reaction temperature. However, the temperature role on toluene conversion was determined to be mild above 450 °C. The product distribution, on the other hand, was extremely affected by temperature, as shown in Table 3. Meshram and Chem<sup>16</sup> reported a similar effect of temperature on toluene conversion using ZSM-5 zeolites. It was determined that the conversion was not sensitive to temperature changes above 500 °C. However, the amount of benzene was constantly increasing with temperature.

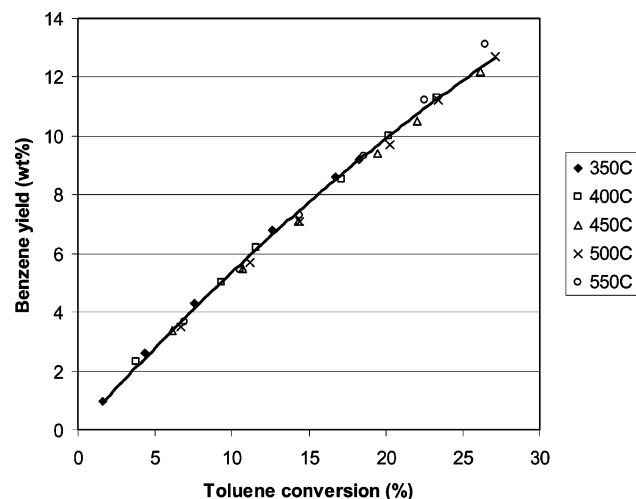


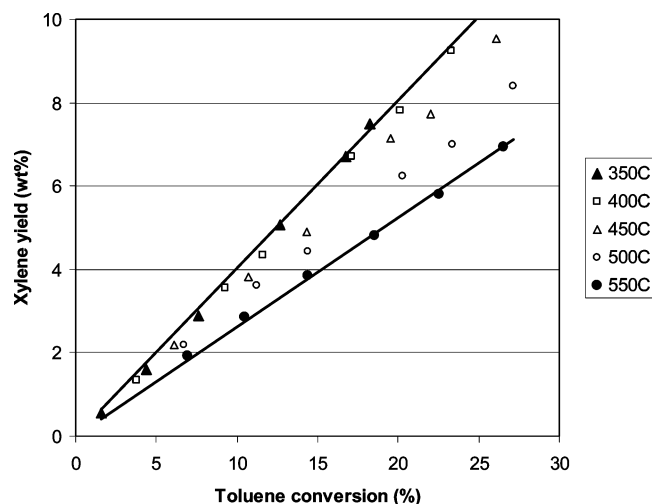
Figure 2. Benzene yield versus toluene conversions at various temperatures: (◆) 350 °C, (□) 400 °C, (△) 450 °C, (×) 500 °C, and (○) 550 °C.

Toluene transformation produces mainly benzene and xylene isomers (equilibrium distribution) and small amount of gases and TMB at low temperature (350 °C). This result suggests that, at low temperature, toluene mainly transforms through disproportionation and the secondary reactions (xylene transalkylation and xylene dealkylation) are not significant. Since benzene is produced by both primary and secondary reactions, it is not surprising to see the benzene yield increasing at all reaction times and temperatures (Figure 2).

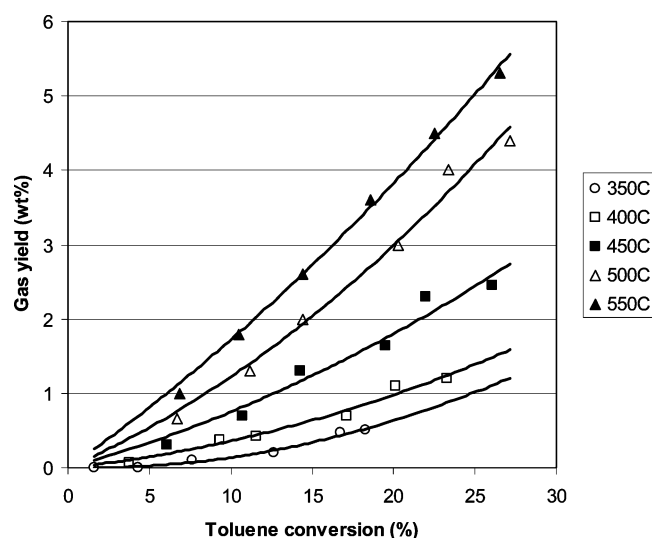
Figure 3 shows the xylene yield as a function of both conversion and temperature. It is clear that the slope is highest at 350 °C and then starts to decrease with increasing temperature, reaching a minimum at 550 °C. This behavior suggests the consumption of xylenes by dealkylation at higher temperatures. A similar result was found by Cejka et al.<sup>29</sup> with a TMB reaction, when tetramethylbenzene (a disproportionation product) was observed to decrease with temperature. Table 3 reveals the low yield of TMB, which rules out any significant consumption of xylenes via disproportionation. This result is in agreement with Uguina et al.<sup>15</sup>

As shown in Figure 4, it is clear that gas yields increase with both contact time and reaction temperature. The temperature effect on gas yield was considerable. For example, at 20% conversion, the gas yield is 0.5 wt % and 3.7 wt % at 350 °C and 550 °C, respectively. Thus, increasing reaction temperature from 350 °C to 550 °C has increased gas yield 7-fold. Furthermore, at these temperatures, the xylene yield, as shown in Figure 3, is 7.7 wt % and 5 wt % at 350 °C and 550 °C, respectively. It can be seen that the xylene yield decreases with temperature, while the gas yield increases. Figure 5 shows that, at constant toluene conversion (18%), the influence of reaction temperature on gases yield is opposite to that on the xylene yields. This suggests that, as the temperature increases, the secondary xylenes dealkylation reaction rate also increases,

(29) Cejka, J.; Katrola, J.; Krejci, A. *Appl. Catal., A* **2004**, 277, 191.



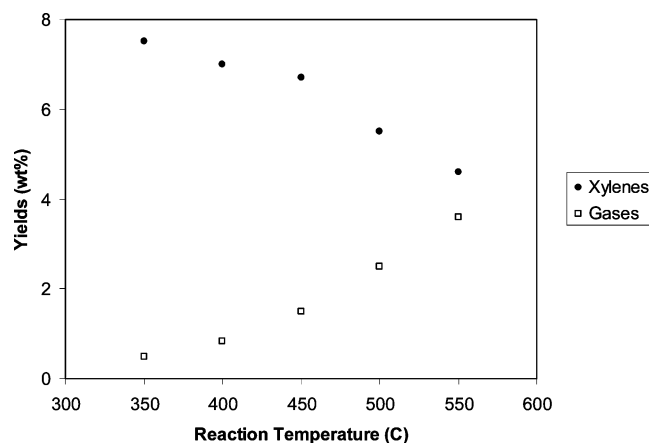
**Figure 3.** Xylene yield at various temperatures: (▲) 350 °C, (□) 400 °C, (△) 450 °C, (○) 500 °C, and (●) 550 °C.



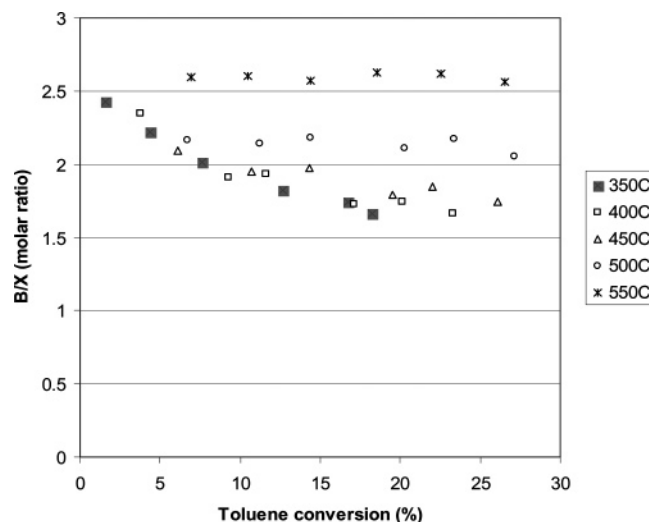
**Figure 4.** Gas yield versus toluene conversion at different temperatures: (○) 350 °C, (□) 400 °C, (■) 450 °C, (△) 500 °C, and (▲) 550 °C.

producing more gases. An analysis of the gas content shows that it includes mainly paraffin gases: ~60 wt % propane and 35 wt % butane. Because no appreciable amount of C1 and C2 gases are found in the product, it can be said that no significant monomolecular dealkylation for either toluene or xylene occurs under our reaction conditions. Thus, it seems that the formation of these gases proceeds via paring reaction.<sup>24,29</sup> Because TMB yield is not significant under our reaction conditions, this would strengthen the suggestion that xylene dealkylation is a very important reaction and its rate increases drastically with temperature.

As the temperature increases, a change in product distribution is noticed. The benzene/xylene ratio (B/X) increases proportionally with temperature, as shown in Figure 6. A similar trend for B/X with temperature was observed by several researchers.<sup>16,20,22</sup> It is depicted in Figure 6 that the B/X ratio is maximum at low toluene conversion and decreases as the conversion increases. This result suggests that toluene dealkylation might be a primary reaction, producing benzene and gas, which explains the initially high B/X value. Bhaskar and Do<sup>20</sup> have observed similar behavior for the B/X ratio at low conversion. They attributed this trend to the high dealkylation rate of xylenes at low toluene conversion. However, as conver-



**Figure 5.** (□) Gas yield and (○) xylene yield versus reaction temperature (at constant toluene conversion of 18 wt %).

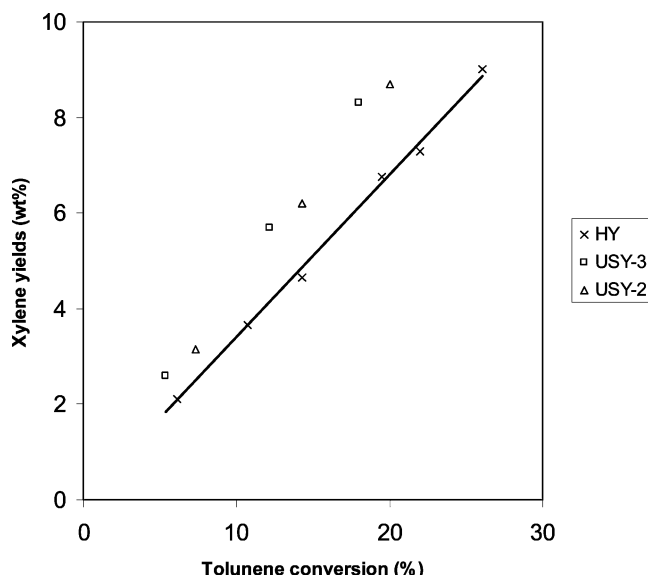


**Figure 6.** Molar ratio of benzene to xylenes (B/X) at different temperatures: (■) 350 °C, (□) 400 °C, (△) 450 °C, (○) 500 °C, and (\*) 550 °C.

sion increases, the xylene concentrations also increase and the xylene dealkylation becomes more prominent.<sup>15</sup> Thus, two dealkylation reactions might occur: a primary toluene dealkylation and a secondary xylene dealkylation. Both dealkylation reactions have a crucial role on the B/X ratio. At much higher temperature (550 °C), the B/X ratio seems to be constant and not a function of conversion. It is relevant to mention that most researchers<sup>16,20,22</sup> have reported B/X ratios greater than unity.

The coke was also measured under different conditions. Table 4 reveals the amount of coke deposition. It is clear that this amount varies with the reaction conditions. However, the ratio of coke wt % to toluene conversion is almost constant and equal to 0.065 under all reaction conditions. This is the basis of the reactant conversion decay model,<sup>30</sup> which will be used in the present study.

**3.3. Comparison between H-Y, USY-2, and USY-3 Catalysts.** A comparison study was conducted using USY-2 and USY-3 with lower acidity than H-Y and higher acidity than USY-1 catalyst. Table 2 shows that the toluene conversion increases as the acidity increases. The catalyst activity is in the following order: H-Y > USY-3 > USY-2 > USY-1. Furthermore, Y-zeolite acidity must be >0.05 mmol/g to get an appreciable toluene conversion. However, toluene conversion



**Figure 7.** Comparison between xylene yields for different catalysts: (x) H-Y, (□) USY-3, and (Δ) USY-2.

**Table 4.** Coke Formation for Toluene Conversions under Different Reaction Conditions over H-Y

temperature/time	conversion (%)	coke amount (wt %)	coke amount (wt %) / conversion (%)
400 °C/5 s	9.3	0.57	0.06
400 °C/7 s	11.6	0.77	0.07
400 °C/10 s	17.1	0.93	0.06
400 °C/15 s	23.3	1.42	0.06
450 °C/5 s	10.7	0.65	0.06
450 °C/7 s	14.3	0.93	0.07
450 °C/10 s	19.5	1.1	0.06
450 °C/15 s	26.1	1.53	0.06
500 °C/5 s	11.2	0.8	0.07
500 °C/7 s	15.3	1.1	0.07
500 °C/10 s	20.25	1.38	0.07
500 °C/15 s	27.12	1.67	0.06

does not necessarily mean disproportionation. Figure 7 shows a comparison between the xylene yields, which can be used as an indicator for disproportionation reaction for these catalysts under the same conditions. It can be seen from this figure that, although toluene conversion increases with acidity, the disproportionation reaction decreases. Thus, it can be concluded that Y-zeolite acidity controls toluene conversion as well as reaction selectivity. To have an appreciable toluene conversion in the present experimental conditions, the acidity must increase from 0.033 mmol/g to 0.1 mmol/g. It is important to note that our experimental conditions involve no hydrogen, and our catalysts were not impregnated by any metal.

**3.4. Kinetic Modeling.** The disappearance of toluene in the Riser Simulator (batch reactor) can be represented by the following equation:

$$\frac{-V}{W_c} \frac{dy_A}{dt} = k'_0 \exp\left[\frac{-E_R}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \varphi y_A \quad (1)$$

where  $T_0$  is the average temperature used during the reaction experiments,  $y_A$  the toluene mass fraction, and  $E_R$  the activation energy. The reactor volume is denoted as  $V$  and  $W_c$  is the mass of catalyst;  $\varphi$  is the intrinsic decay function. Several models have been used to account for catalyst decay. One of the most well-known is the time-on-stream (TOS) model.

**3.4.1. Time-on-Stream (TOS) Model.** One classical approach while describing catalyst decay is to consider catalyst decay as a function of the TOS. A classical relationship

**Table 5.** Kinetic Constants for Toluene Conversion (over H-Y), Based on the Time-on-Stream (TOS)

parameter	value	95% CFL
$k'_0$ (cm <sup>3</sup> /g-cat s)	1.32	0.13
$E_R$ (kcal/mol)	3.47	0.50
$\alpha$ (s <sup>-1</sup> )	0.02	0.02
$r^2$	0.98	

is that proposed by Voorhies:<sup>31</sup>

$$\varphi = \exp(-\alpha t) \quad (2)$$

where  $\alpha$  is a constant and  $t$  is the time the catalyst is exposed to a reactant atmosphere (the time-on-stream, TOS).

By substituting eq 2 into eq 1 and integrating the resulting equation, the following is obtained:

$$y_A = \exp\left\{-\frac{W_c k'_0 \exp\left[\frac{-E_R}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]}{V\alpha} [1 - \exp(-\alpha t)]\right\} \quad (3)$$

When the decay model based on the TOS, in the context of the riser simulator, was established (eq 3), it was tested under several operating conditions, as follows: (a) six different reaction times (3, 5, 7, 10, 13, and 15 s), (b) four different temperatures (350, 400, 450, and 500 °C), and (c) a single catalyst/feed ratio (catalyst/feed = 5).

The three model parameters  $k'_0$ ,  $E_R$ , and  $\alpha$  were determined using nonlinear regression (MATLAB package). Table 5 reports the parameters obtained and the limited spans for the 95% confidence interval. Figure 8 shows the comparison of the experimental and model predicted conversions (eq 3). In addition, Figure 9 reports the random distribution of residuals between the experiments and the modeling conversions.

**3.4.2. Reactant Conversion (RC) Model.** It was demonstrated by Al-Khattaf and de Lasa<sup>30</sup> that a catalyst activity decay function can be conveniently expressed as a function of the converted reactant. This decay model relates catalyst deactivation to the extent of conversion and have been successfully tested for modeling 1,2,4-trimethylbenzene,<sup>32</sup> xylene reactions,<sup>27</sup> the cracking of cumene,<sup>30</sup> and 1,3,5-tri-isopropylbenzene.<sup>33</sup>

This model was developed based on following equation:

$$\frac{dX_C}{dy_A} = A \quad (4)$$

where  $A$  lumps a group of constant parameters and  $X_C$  is the mass fraction of coke, based on the catalyst weight.

By integrating eq 4 between 0 and  $X_C$  and between 1 and  $y_A$ , the following equation is obtained:

$$X_C = A(1 - y_A) \quad (5)$$

with

$$A = -\frac{\nu_c W_{hc} M W_c}{W_c M W_A} \quad (6)$$

After this first step of relating the conversion of reactant to the coke fraction is established, the next step in the analysis is to consider a catalyst activity decay function based on the

(31) Voorhies, A., Jr. *Ind. Eng. Chem.* **1945**, 37, 318.

(32) Atias, J. A.; Tonetto, G.; de Lasa, H. *Ind. Eng. Chem. Res.* **2003**, 42, 4162–4173.

(33) Al-Khattaf, S.; Atias, J.; Jarosch, K.; de Lasa, H. I. *Chem. Eng. Sci.* **2002**, 57, 4909.

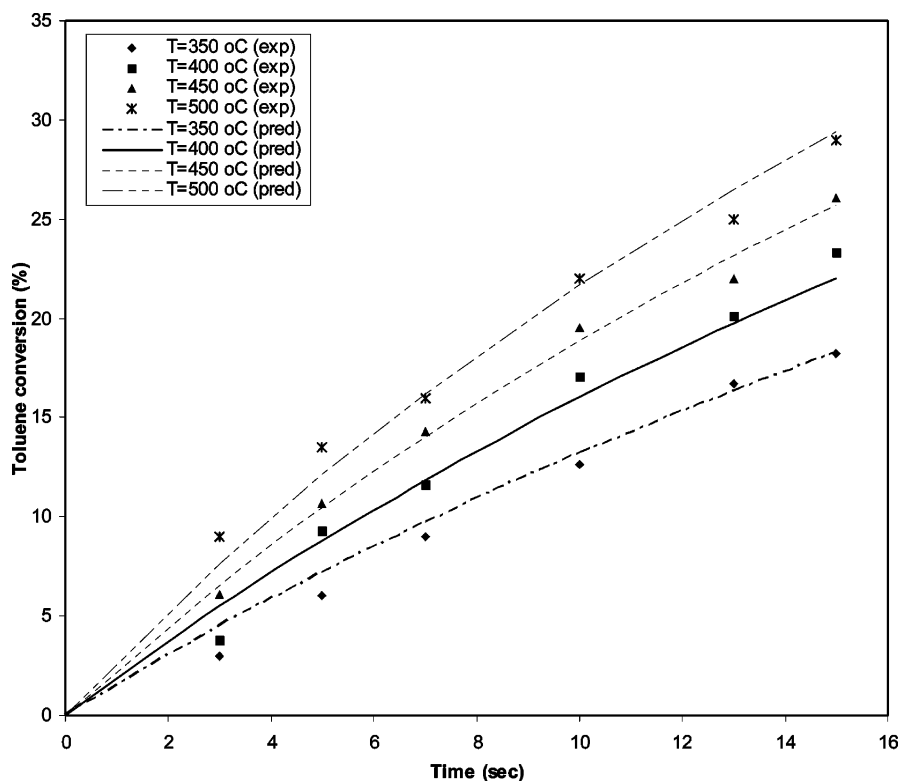


Figure 8. Modeling toluene conversion over H-Y; the decay function is based on the time-on-stream (TOS).

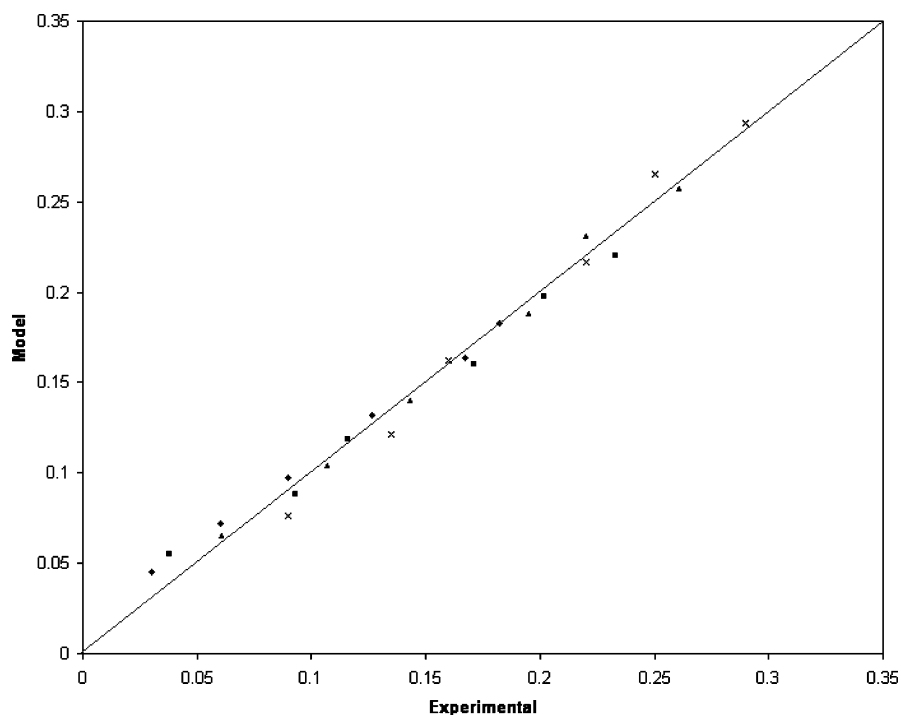


Figure 9. Overall comparison between the experimental results and model predictions (based on the time-on-stream, TOS): (◆) 350 °C, (■) 400 °C, (▲) 450 °C, and (×) 500 °C.

concentration of coke, as proposed by Froment and Bischoff:<sup>34</sup>

$$\varphi = \exp(-\delta X_C) \quad (7)$$

However, given the relationship between the coke concentration on catalyst ( $X_C$ ) and the weight fraction of toluene ( $y_A$ ), as given

by eq 5, the following equation is obtained:

$$\varphi = \exp[-\lambda(1 - y_A)] \quad (8)$$

where

$$\lambda = A\delta \quad (9)$$

The obtained result can be substituted in eq 1 and the following equation, which describes the rate of reaction

(34) Froment, G. F.; Bischoff, K. B. *Chemical Reactor Analysis and Design*, Second Edition; Wiley: New York, 1979.



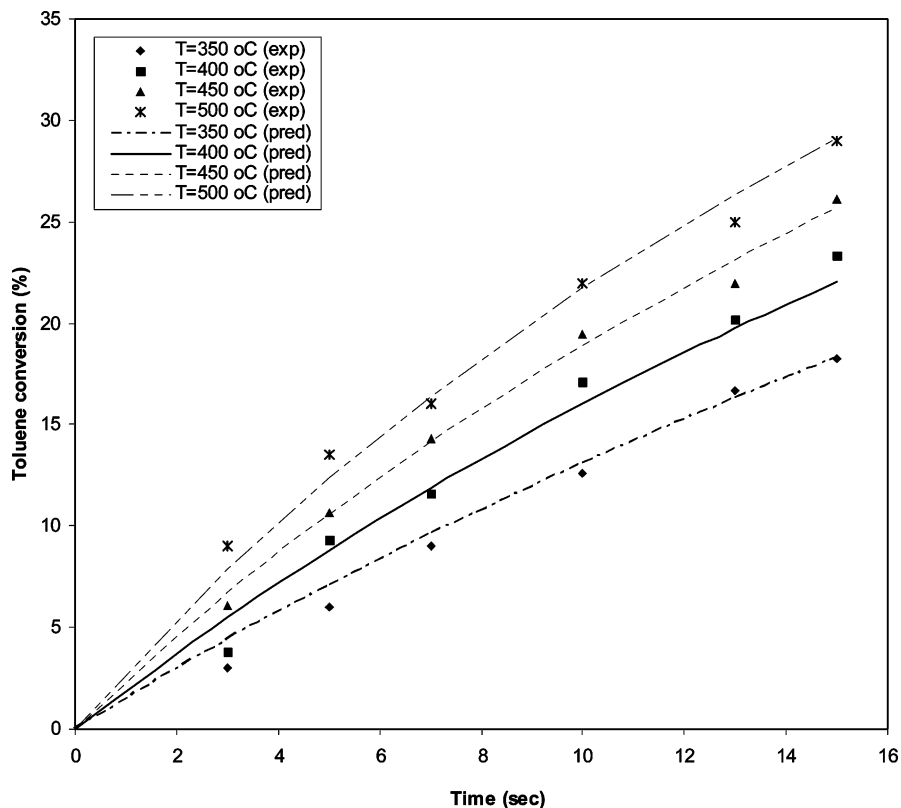


Figure 10. Modeling toluene conversion over H-Y; the decay function is based on the reactant converted (RC) model.

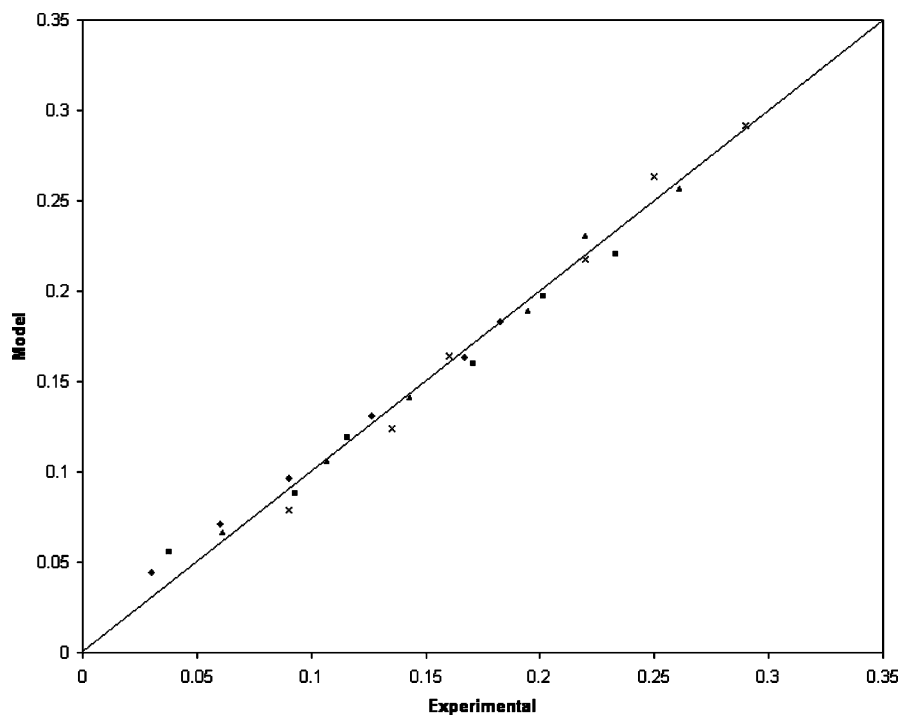


Figure 11. Overall comparison between the experimental results and model predictions (RC): (◆) 350 °C, (■) 400 °C, (▲) 450 °C, and (×) 500 °C.

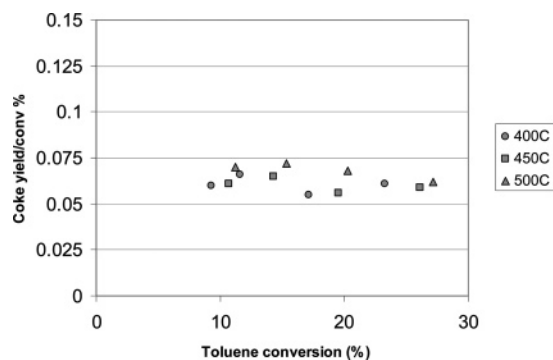
consumption, is obtained:

$$\frac{-V}{W_c} \frac{dy_A}{dt} = k'_0 \exp \left[ \frac{-E_R}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \exp[-\lambda(1 - Y_A)y_A] \quad (10)$$

Thus, the catalyst activity decay model based on reactant conversion given by eq 10 involves three parameters:  $k'_0$ ,  $E_A$ , and  $\lambda$ .

Following this step, a nonlinear regression involving eq 10 with three adjustable parameters was considered, using MATLAB software. Table 6 reports the set of parameters obtained and the limited spans for the 95% confidence interval. Figures 10 and 11 report the comparisons of the model results.

Regarding the activity decay model, based on reactant conversion, one main assumption is given by eq 4. In fact, one main consideration of the model is that  $A$  is a constant parameter



**Figure 12.** Coke yield/(toluene conversion) versus toluene conversion: (●) 400 °C, (■) 450 °C, and (▲) 500 °C.

**Table 6.** Kinetic Constants (over H-Y), Based on Reactant Conversion (RC)

parameter	value	95% CFL
$k'_0$ (cm <sup>3</sup> /g-cat s)	1.22	0.12
$E_R$ (kcal/mol)	4.0	0.16
$\lambda$	1.5	0.95
$r^2$	0.99	

that is not affected by toluene conversion:

$$A = \frac{X_C}{(1 - y_A)} \quad (11)$$

To check the validity of this assumption, several independent runs were developed and in each of them, in addition to the measurement of toluene conversion, the amount of coke that formed was determined. On this basis, the  $X_C/(1 - y_A)$  group was calculated for each run independently. It was observed that, as reported in Table 4,  $A = 0.065 \pm 0.007$  for the different temperatures and contact times used in the study. The confidence limits for  $A$  are approximately  $\pm 10\%$ , mainly as a result of uncertainty on the measurement of  $X_C$  concentration on the catalyst. The  $A$  parameter can be assumed to be constant (see Figure 12), and this validates the process of numerical integration of eq 10 that has been adopted to calculate the parameters  $E_R$ ,  $k'_0$ , and  $\lambda$ .

Finally, and considering that the determined  $\lambda$  parameter was 1.5 and adopting a value of  $A = 0.07$ , then it results that  $\delta = 23.1$ . Thus, eq 7 can be also reported as

$$\varphi = \exp(-23.1X_C) \quad (12)$$

It can be also mentioned that  $X_C$  for toluene transformation (under the present reaction conditions) has a typical value in the mass-fraction range of 0.01–0.02. Then, at  $X_C = 0.015$ ,  $\varphi = 0.70$  (or 30% of the catalyst activity is lost) at a concentration of 0.15 g coke/g catalyst.

In summary, the model developed as a function of toluene conversion, in the context of the present study, is shown to be adequate for predicting toluene conversion for a large range of conversions, temperatures, and reaction times. It should be stressed that this decay model was developed for these reaction conditions free of transport constraints and, in this context, it can be considered an “intrinsic decay function” model that can be applied to the transformation of other hydrocarbon species on the same type of Y-zeolites.

## 4. Conclusions

The following conclusions can be drawn from the catalytic transformation and modeling of toluene over the present catalyst in the riser simulator under the conditions of the experimental study:

(1) The conversion of toluene was determined to increase with contact time and temperature. It was observed that the secondary xylene dealkylation reaction becomes vital at high temperatures, leading to the increase in benzene/xylene (B/X) ratio and gases. The yield of trimethylbenzene (TMB) was not observed to be significant, which indicates that the secondary transalkylation reactions between two xylene molecules or between a toluene molecule and a xylene molecule do not occur to an appreciable extent.

(2) It was determined that Y-zeolite acidity has complete control of the toluene reactions. To have an appreciable conversion, the acidity must be  $>0.05$  mmol/g. Acidity in the range of 0.1–0.2 mmol/g favors the disproportionation reaction, producing more xylenes, whereas an acidity of  $>0.2$  mmol/g favors the dealkylation reaction, producing more gases.

(3) The toluene conversion reaction was modeled using two different deactivation functions. One function is based on the time-on-stream (TOS) deactivation, and the other is based on reactant conversion. Both models have resulted in similar kinetic constants. The parameters optimized to the experimental data gave a good prediction of the overall reaction kinetics for toluene transformation in our experimental conditions. Thus, providing significant evidence that the “reactant converted” decay model can be adequately utilized to account for the catalyst deactivation in similar reaction systems.

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## Nomenclature

- $C_i$  = concentration of species  $i$  in the riser simulator [mol/m<sup>3</sup>]  
 CFL = confidence limit  
 $E_i$  = apparent activation energy of the  $i$ th reaction [kJ/mol]  
 $k$  = apparent kinetic rate constant [m<sup>3</sup> kg-cat<sup>-1</sup> s<sup>-1</sup>];  $k = k'_0 \exp\{-(-E_R/R)[(1/T) - (1/T_0)]\}$   
 $k'_0$  = pre-exponential factor in the Arrhenius equation, defined at an average temperature [m<sup>3</sup> kg-cat<sup>-1</sup> s<sup>-1</sup>] (units based on first-order reaction)  
 $MW_i$  = molecular weight of species  $i$   
 $r$  = correlation coefficient  
 $R$  = universal gas constant [kJ kmol<sup>-1</sup> K<sup>-1</sup>]  
 $t$  = reaction time [s]  
 $T$  = reaction temperature [K]  
 $T_0$  = average temperature of the experiment;  $T_0 = 698$  K  
 $V$  = volume of the riser [45 cm<sup>3</sup>]  
 $W_c$  = mass of the catalysts;  $W_c = 0.81$  g-cat  
 $W_{hc}$  = total mass of hydrocarbons injected in the riser;  $W_{hc} = 0.162$  g  
 $y_i$  = mass fraction of the  $i$ th component [wt %]

## Greek Letters

- $\alpha$  = apparent deactivation constant [s<sup>-1</sup>] (TOS model)  
 $\varphi$  = apparent deactivation function

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