

Synthesis of xylene over cerium modified large pore zeolite: A kinetic study

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Synthesis of xylene by transalkylation of 1, 2, 4 trimethylbenzene with toluene over cerium modified beta zeolite has been investigated in the present study. The reaction has been carried out in a fixed bed down-flow reactor. The effect of various process parameters: temperature (623-723K), reactant ratio (0.5-4) and space time (0.88-2.9 kg h/kmol), on the toluene conversion and xylene selectivity are investigated. Zeolites with different amount of cerium loading (4.12 wt%, 6.54 wt%, 8.1 wt% and 10.34 wt%) have been prepared and characterized. Zeolite having 8.1wt% cerium loading is proved to be the most active catalyst. Maximum toluene conversion of 58.77% is achieved at a temperature-698K, reactant ratio-3:1, space time-2.9 kg h/kmol. The kinetic runs have been carried out to choose the zone in which the mass transfer effects are negligible. Based on product distribution, a mechanism for the formation of xylene over the modified catalyst is proposed along with a rate expression. The kinetic and adsorption constants of the rate equations are estimated by non-linear regression. The activation energy is found to be 122.41 kJ/mol which compares well with those reported in the literature for transalkylation reaction over similar catalysts.

Keywords: Beta zeolite, Cerium, Kinetic modeling, Transalkylation, Xylene

Global demand for xylene is growing sharply over the last decade. In the year 1999, the world consumption of mixed xylene was about 24 million tons and is expected to grow at a rate of 6.2% to 35.9 million tons by the year 2007 and it will reach upto 70.5 million tons in 2020. Asia Pacific is expected to account for 81.5% of the global xylene demand in 2020. Among the three xylene isomers, *p*-xylene is the commercially important product and thus most expensive, followed by *o*-xylene. This indicates that xylenes will have considerable importance in the commercial market. The majority (more than 90 percent) of mixed xylene isomers are used for blending into petrol as an octane additive and for the production of terephthalic acid, polyethylene terephthalate, phthalic anhydride, pharmaceuticals, perfumes, fabricated items, pesticide formulations¹⁻⁴. Transalkylation and disproportionation are the two prominent processes for the interconversion of aromatics especially for the production of dialkylbenzenes like xylene³⁻⁶.

The traditional Friedel-Craft catalysts for transalkylation and alkylation reactions are various mineral acids such as HF, and H₂SO₄ or Lewis acid such as AlCl₃, and BF₃. The use of these substances involves environmental and technological problems due to difficulty of recycling and separation from the

product and their corrosive nature. The present tendency is to replace these conventional catalysts by solid acids like zeolites which can exhibit acidities close to those of traditional mineral acid solution. Among the zeolites, large pore zeolites like X, Y, beta, mordenite are the most effective whereas small and medium pore zeolites like zeolite A, ZSM-5 are not much effective for catalysing transalkylation reaction due to diffusional resistance^{4,7}. Transalkylation of large size TMB molecule is favoured only by large pore zeolite^{4,5,8-10}.

Higher the acidity of a zeolite higher is its activity^{8,11}. The number and strength of the acid sites can be increased to a great extent by exchanging cations of the zeolite with some metal ions¹². It is reported that replacement of sodium or hydrogen ions of zeolite with polyvalent cations (La, Ce, Cu, Ni, Pt etc.) imparts superior catalytic activity to the zeolites by increasing its acidity^{1,13,14}. This increased activity of modified zeolite is due to the exchange of monovalent cations with polyvalent cations which lead to the formation of concentrated acidic sites rather than dispersed acidic sites. Out of various rare earth metals, cerium in its +4 ionic state may lead to the formation of highly concentrated acidic sites formed by replacement of four H⁺ ions.

Recently, transalkylation reaction of commercial heavy reformates (TMB) was reported under industrially relevant conditions over seven different acid zeolite catalysts with channel systems containing 10 MR, 12 MR pores. Zeolites were impregnated with seven different metals (Re, Pt, Mo, Ga, Ni, La, Bi). Zeolite pore size and geometry were found to have a direct influence on dealkylation and transalkylation of the different alkyl groups¹³. The conversion of heavy reformates to xylenes was reported over H-mordenite catalysts with different Si/Al ratios⁸. Zeolites beta, mordenite and zeolite Y were evaluated for their activity in transalkylation reaction of toluene with trimethylbenzenes⁹. Zeolite beta was found to possess the highest activity compared with mordenite and zeolite Y. Zeolite Beta with the lowest Si/Al ratio of 12.5 exhibited the highest xylene yield. There is very scarce literature available on the modification of beta zeolite with rare earth metals for transalkylation by which xylene production can be maximized in a controlled process condition. Therefore, objective of the present work was to maximize the production of commercially important xylene in transalkylation of toluene with trimethylbenzene over cerium modified beta zeolite catalyst and to propose a model for the reaction system and to estimate the model parameters.

Experimental Section

Materials and reagents

Beta zeolite in the form of 1.5 mm extrudates used in present study was obtained from Sud chemie, Vadodara. Ceric ammonium nitrate for cerium exchange was supplied from CDH chemicals, India. Toluene was procured from M/s Merck chemical, India and trimethylbenzene (TMB) was obtained from Sigma Aldrich Pvt. Ltd., India.

Catalyst Preparation and characterization

The commercially available H-beta zeolite was modified by exchanging the sodium ions with cerium (+4) ions. Modification of commercial zeolite was done, as the sodium form of zeolites is known to be catalytically less active. The beta zeolite was first calcined at 623 K for 3 hr to remove moisture and kept ready for cation exchange. The catalyst particles were refluxed with required percentage of ceric ammonium nitrate at 363 K for 24 hr, thereby modifying H form of beta zeolite into Ce-beta form. The modified catalyst particles were washed and filtered many times with deionized water and then

dried at 393 K for 14 h. Finally, it was calcined for 4 h at 723 K. Catalysts treated with 6, 8, 10 and 12% ceric ammonium nitrate solutions were designated as CeB₆, CeB₈, CeB₁₀ and CeB₁₂ respectively.

Temperature programmed desorption (TPD) of ammonia

Ammonia TPD of the modified catalysts was performed in a CHEM-BET 3000 instrument (Quantachrome). In a typical experiment, 0.1 g of the catalyst sample was first degassed at 723K for 1 hr with a nitrogen flow followed by cooling to low temperature (~273K). A gas mixture of nitrogen and ammonia, consisting of about 1 mol% ammonia and rest nitrogen, was then passed through the sample for 1 hr. The catalyst sample was then heated to 293K and kept at that temperature until the steady state was attained. The sample was then heated from 293K to 973K at a heating rate of 10 K/min. The desorbed ammonia was detected by a TCD analyzer. The TPD profiles of modified zeolites are shown in Fig. 1. Desorption of ammonia corresponding to different peaks is indicative of energy levels at which ammonia is bound to acid sites. The profiles indicate that the catalysts contain mainly two types of acid sites of varying strengths. The strengths of the acid sites increase with Ce-exchange as the desorption peaks shift gradually towards the higher temperatures with increasing cerium content of the catalysts. The acidity and cerium content of various catalysts are shown in Table 1.

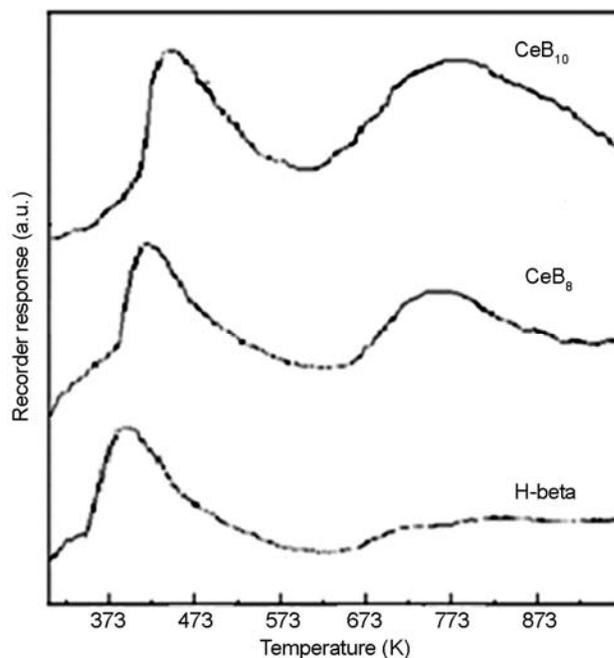


Fig. 1 —TPD of H-beta and cerium modified beta zeolite

Table 1—Cerium content and acidity of various catalysts

Catalyst	Cerium (wt%)	Acidity (mmol/g)
H-beta	NIL	0.88
CeB ₆	4.12	1.19
CeB ₈	6.54	1.42
CeB ₁₀	8.10	1.79
CeB ₁₂	10.34	1.94

Experimental procedure and product analysis

Transalkylation reaction was carried out in fixed-bed, continuous down-flow, stainless steel (SS 316) reactor. The reactor was fitted with a preheater in the upstream and a condenser in the downstream. The zeolite catalyst (2 g) was loaded into the reactor which was supported on a wire mesh at the centre of reactor. The catalyst was activated for 3 h in nitrogen atmosphere before the experimental runs were started. The reaction temperature was measured using a thermocouple placed in a thermowell extending from the top of the reactor to the centre. All experimental runs were carried out at atmospheric pressure. Toluene-TMB (feed) mixture was introduced into the reactor using a metering pump through the preheater. The product vapors along with unreacted reactants were condensed in a condenser and the liquid samples collected were analyzed in a Gas Chromatograph (Bruker) using a flame ionisation detector (FID).

The conversion of toluene and selectivity of xylene were calculated according to following formulae:

$$\text{Toluene conversion} = \frac{(\text{Toluene in feed} - \text{Toluene in product})}{\text{Toluene in feed}} \times 100$$

$$\text{Xylene selectivity} = \frac{\text{Xylene in product mixture}}{\text{Aromatics in product excluding Toluene and Trimethylbenzene}} \times 100$$

$$\text{Xylene yield} = \frac{\text{Xylene in product mixture}}{\text{Aromatics in the reaction mixture}} \times 100$$

The transalkylation reaction of toluene with trimethylbenzene is usually accompanied by a number of reactions like isomerisation, disproportionation and dealkylation. Isomerisation reaction involves isomerisation of 1,2,4 TMB to 1,2,3 and 1,3,5 TMB; and isomerisation of para xylene to *ortho* or *meta* xylene. Two molecules of trimethylbenzene can react together to form xylene and tetramethylbenzene (TeMB) whereas the disproportionation reaction of toluene yields benzene and xylene.

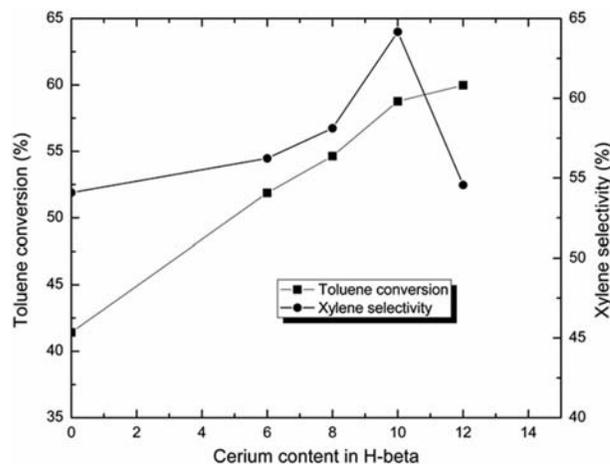


Fig. 2—Effect of cerium content on toluene conversion and xylene selectivity. Temperature-698K; TMB to toluene ratio-3:1; space time-2.9 kg h/kmol; N₂ to feed rate-0.16

Results and Discussion

Kinetic runs

Effect of cerium loading and time-on-stream

The effect of cerium loading on toluene conversion and xylene selectivity is shown in Fig. 2. The toluene conversion was found to increase with increase in cerium content. The toluene conversion over CeB₁₂ was comparable with the conversion over CeB₁₀ but the xylene selectivity decreased over CeB₁₂ due to the formation of side products due to presence of high acidic sites.

The stability of modified H-beta zeolites and unmodified H-beta zeolite was tested for three hours time-on-stream at 698K and atmospheric pressure. The toluene conversion remained almost constant during first 1 hr time period as shown in Fig. 3. It is seen from this figure that CeB₁₀ zeolite gives much higher conversion than rest of catalysts. As the time increased, conversion of toluene decreased due to the deactivation of zeolite at longer time. Therefore, CeB₁₀ was chosen for further studies.

Effect of temperature

The effect of temperature on product distribution was investigated at different temperatures in the range of 623K-723K over CeB₁₀ catalyst. All the other parameters were kept unchanged. The product distribution varied with changing temperature as shown in Table 2. The conversion of toluene is maximum (58.77%) at 698K and then decreases to 50% at temperature of 723K. This decrease in conversion is due to deactivation of catalyst by coke formation. This is evident from the product

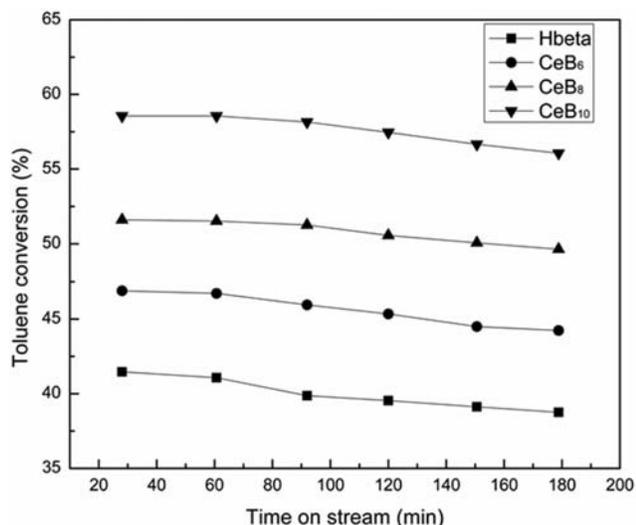


Fig. 3—Effect of time on stream on toluene conversion and xylene yield. Temperature-698K; TMB to toluene ratio-3:1; space time-2.9 kg h/kmol; N₂ to feed rate-0.16

Table 2—Transalkylation product distribution at different temperatures

Temperature (K)	623	648	673	698	723
<i>Product distribution (wt%)</i>					
Benzene	0.94	1.34	1.87	2.56	2.23
Toluene	14.28	11.33	9.07	8.41	10.2
Xylene					
<i>Para</i>	10.51	15.24	16.9	18.44	19.1
<i>Ortho</i>	1.84	4.79	6.66	9.58	10.07
TMB					
1,3,5-	5.01	4.28	4.94	5.01	5.71
1,2,4-	61.03	55.94	53.15	47.93	43.45
1,2,3-	3.41	3.72	3.86	3.96	4.53
TeMB	2.98	3.36	3.91	4.11	4.71
Toluene conv.(wt%)	30.01	44.46	55.53	58.77	50.00
TMB conv.(wt%)	23.32	29.72	33.28	39.78	45.41
Xylene yield (wt%)	15.21	21.03	23.56	28.02	29.17
Xylene selectivity (wt%)	50.02	60.09	61.77	64.17	62.94

TMB to toluene ratio-3:1; space time-2.9 kg h/kmol; N₂ to feed ratio-0.16

distribution that with increase in temperature, formation of side products is increased; xylene selectivity is decreased but the xylene yield increased with increase in temperature.

Effect of TMB to toluene mole ratio

In the transalkylation reaction the TMB to toluene ratio was varied from 0.5 to 4 at a reaction temperature of 698K and space time of 2.9 kg h/kmol. From the Fig. 4, it is seen that the maximum toluene conversion is obtained at a TMB to toluene ratio 3:1 above which conversion of toluene decreases.

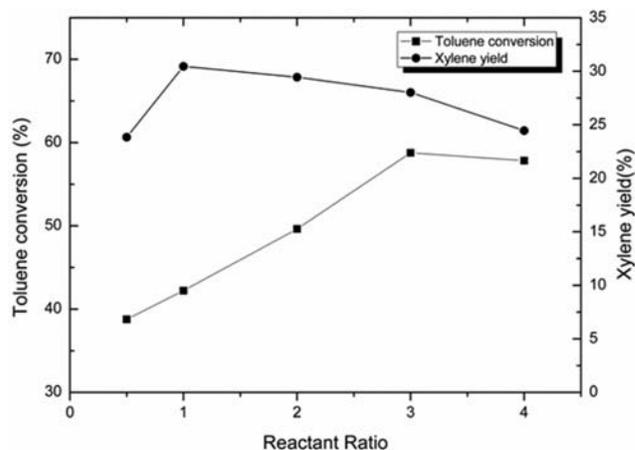


Fig. 4—Effect of reactant ratio on toluene conversion and xylene yield. Temperature-698K; space time-2.9 kg h/kmol; N₂ to feed rate-0.16

At higher mole ratio of TMB to toluene, all the active sites of the catalysts are blocked by the excess reactant. Less availability of toluene as limiting reactant decreases the conversion of toluene at higher mole ratio. The xylene yield is less when TMB is taken as limiting reactant due to less availability of number of alkyl groups in the system. However, at TMB to toluene mole ratio of 1:1, xylene yield is maximum but further increase of TMB in the reactant leads to the formation of more side products like TeMB.

Effect of space time

The effect of space-time was studied in the range of 0.88–2.9 kg h/kmol. The toluene conversion increased with increase in space time as shown in Fig. 5. This may be due to a higher contact time between the reactant and the catalyst. Initially, xylene selectivity increased with space time, however, at much higher space time, xylene selectivity decreased due to the formation of undesired products.

Mass transfer considerations

Any kinetic study should be done in negligible mass transfer resistance during the reaction. Experiments were carried out to estimate the external diffusional effects, with same catalyst size and constant space-time for different feed rates. The results shown in Table 3 indicate that the conversion of toluene is same at all three values of W/F. Therefore, the external mass transfer resistance is negligible.

Experiments were also carried out to test the intraparticle diffusional limitations by varying the catalyst particle size while keeping space-time constant.

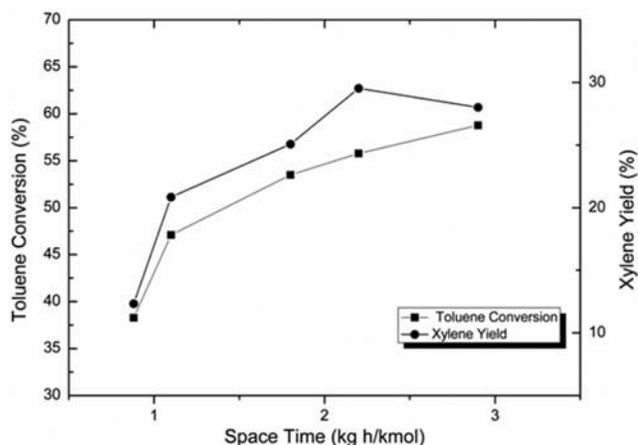


Fig. 5—Effect of space time on toluene conversion and xylene yield. Temperature-698K, TMB to toluene ratio-3:1, N₂ to feed rate-0.16

Table 3—Effect of external diffusional resistances on conversion of toluene

Space-time (kg h/kmol)	Conversion of toluene (%)	
	Catalyst weight = 0.002 kg	Catalyst weight =0.004 kg
1.1	14.56	14.11
1.8	20.13	20.01
2.2	24.19	23.98

Temperature-623K; TMB to toluene ratio-3:1; CeB₁₀ (1.5 mm) catalyst; N₂ to feed ratio-0.16

Table 4—Effect of intraparticle diffusional resistance on toluene conversion

Particle size d _p (mm)	Conversion of toluene (%)		
	Space-time (kg h/kmol) =1.1	Space-time (kg h/kmol) = 1.8	Space-time (kg h/kmol) = 2.2
0.50	14.59	20.54	24.87
1.00	14.56	20.13	24.19
1.50	14.19	20.05	23.98

Temperature-623K; TMB to toluene ratio-3:1; CeB₁₀(0.002kg) catalyst; N₂ to feed ratio-0.16

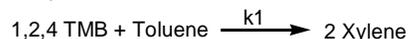
The experimental data obtained are presented in Table 4. From the results it is clear that toluene conversion is independent of the particle, indicating that the particle size used in the present study were within the intraparticle diffusion free range. In zeolite-catalyzed reactions, two types of diffusion processes are involved: micro pore diffusion inside the zeolite crystal and macropore diffusion between the zeolite crystals within the catalyst pellets. The above experiments for mass transfer resistances confirm only the absence of macropore diffusional

resistance. The resistance due to micropore diffusion could not be evaluated, as it required modification of the catalyst synthesis conditions that affect the micropore size of the crystals.

Kinetic modeling

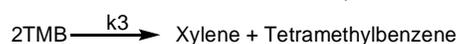
According to the product distribution, the system can be described by the following reactions:

Primary reaction:

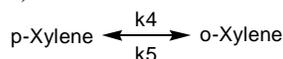


Secondary reactions:

i) Disproportionation reactions:



ii) Isomerisation reactions:



For the rate of disappearance of toluene, Langmuir-Hinshelwood-Hougen-Watson model was attempted to fit the kinetic data.

The rate expressions using L-H-H-W model with surface reaction as the rate controlling step are,

For dual site mechanism:

$$-r_T = dX_T / d = (k_1 K_T K_{TMB} p_T p_{TMB} + k_2 k_T^2 p_T^2) / Z^2 \dots (1)$$

where $Z = 1 + K_{TMB} p_{TMB} + K_T p_T$

For single site mechanism (with TMB in gas phase):

$$-r_T = dX_T / d = (k_1 p_T p_{TMB} + (k_2 / Z) k_T^2 p_T^2) / Z^2 \dots (2)$$

where $Z = 1 + K_T p_T$

For stoichiometric model:

$$-r_T = dX_T / d = (k_1 p_T p_{TMB} + k_2 p_T^2) \dots (3)$$

The partial pressures in the above equations were calculated using the fractional conversions and total pressure, P, as given below,

$$p_T = (1 - X_T) P / 4.64$$

$$p_{TMB} = (3 - X_{TMB}) P / 4.64$$

$$p_{p\text{-xylene}} = (X_{p\text{-xylene}}) P / 4.64$$

$$p_{o\text{-xylene}} = (X_{o\text{-xylene}}) P / 4.64$$

$$p_{1,3,5TMB} = (X_{1,3,5TMB}) P / 4.64$$

$$p_{1,2,3TMB} = (X_{1,2,3TMB}) P / 4.64$$

$$p_{TeMB} = (X_{TeMB}) P / 4.64$$

Table 5—Kinetic and adsorption parameters for dual site

Kinetic and adsorption parameters	Temperature			
	623K	648K	673K	698K
k_1 (kmol/kg h)	1.42	3.20	8.93	16.58
k_2 (kmol/kg h)	0.79	1.81	4.64	13.07
K_T (atm ⁻¹)	2.24	2.01	1.40	1.23
K_{TMB} (atm ⁻¹)	0.94	0.88	0.55	0.23

Table 6—Kinetic and adsorption parameters for single site

Kinetic and adsorption parameters	Temperature			
	623K	648K	673K	698K
k_1 (kmol/kg h)	0.50	1.77	3.65	4.5
k_2 (kmol/kg h)	0.01	1.04	2.52	3.04
K_T (atm ⁻¹)	2.30	1.24	1.18	1.15

Table 7—Kinetic and adsorption parameters for stoichiometric model

Kinetic and adsorption parameters	Temperature			
	623K	648K	673K	698K
k_1 (kmol/kg h)	1.06	2.12	3.28	4.95
k_2 (kmol/kg h)	0.65	1.12	1.37	1.92

A non-linear regression algorithm was used for parameter estimation. The optimum values of the parameters were estimated by minimizing the objective function given by the equation,

$$f = \sum_{i=1}^n [(Rate\ predicted)_i - (rate\ experimental)_i]^2$$

Model selection

The kinetic and adsorption constants evaluated by nonlinear regression are tabulated in Tables 5, 6, and 7. For dual site model with the data reported in Table 5 the estimated error was 8.35×10^{-4} . For single site model with the data reported in Table 6, error estimate was 6.4×10^{-3} . For stoichiometric model with the values of the constants from Table 7, the error was 4.7×10^{-3} . By comparing the standard errors, dual site mechanism model was found to be the best. The experimental and the predicted toluene conversions for this model, at different temperatures, are plotted in Fig. 6. The plot shows a good correlation between the experimental and predicted rates having an R^2 value of 0.96.

The kinetic constants derived from equation (1), were used to found the activation energy (E_a), using the Arrhenius equation,

$$\ln K = \ln A - E_a / RT \quad \dots(4)$$

Table 8—Activation energy and pre-exponential factors for different reactions

Reaction	E_{act} (kJ/mol)	Pre-exponential factor
Transalkylation reaction	122.407	2.4×10^{10}
Toluene disproportionation	135.705	2.1×10^{11}

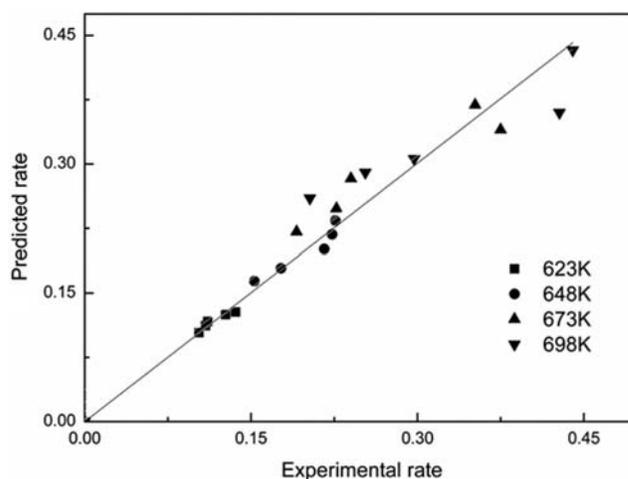


Fig. 6—Experimental versus predicted rate of toluene conversion

Activation energy for transalkylation reaction was estimated to be 122.41 kJ/mol. An apparent activation energy value of 130.2 kJ/mol was reported for the transalkylation reaction of DIPB with benzene with SAPO-5 as the catalyst¹⁵. The value of activation energy varying from 46 to 104.6 kJ/mol in the temperature range 483-543K for the transalkylation of *m*-diethylbenzene over beta zeolite has also been reported¹⁶. The value of frequency factor (A) was found to be 2.4×10^{10} . Activation energy and pre-exponential factors of different reactions are reported in Table 8.

Conclusion

Transalkylation of toluene with TMB is carried out over H-beta and Ce-beta zeolite catalysts. Modification of zeolite with cerium brings significant increase in the activity of catalyst and selectivity of the product. A time on stream study show that the catalyst is quite stable at an operating temperature of about 700 K. Maximum toluene conversion 58.77 % is achieved at a temperature 698K, reactant ratio 3, space time 2.9 kg h/kmol. Based on the product distribution, a reaction mechanism is proposed together with a rate expression for the disappearance of toluene. The kinetic and the adsorption constants of the rate equation are estimated. The activation energy

for transalkylation reaction is determined to be 122.41 kJ/mol, which is comparable with the data reported in the literature for transalkylation reactions.

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