Kinetic analysis of benzene ethylation over ZSM-5 based catalyst in a fluidized-bed reactor

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ABSTRACT

Benzene ethylation has been investigated over fresh ZSM-5 based catalyst in a riser simulator that mimics the operation of a fluidized-bed reactor. Experimental runs for the kinetic study were carried out at four different temperatures (300, 325, 350 and 400 °C) for reaction times of 3, 5, 7, 10, 13, and 15 s. Benzene to ethanol (B/E) mole ratio was varied from 1:1 to 3:1. Benzene conversion, ethylbenzene yield and diethylbenzene yield were found to increase with reaction temperature and time for the different temperatures. The maximum benzene conversion of 16.95% in which the main products were ethylbenzene, diethylbenzene and other hydrocarbon as by-products was obtained over the fresh catalyst at 400 °C. The experimental results were modeled using quasi-steady-state approximation with catalyst deactivation function based on two different models. Kinetic parameters for benzene ethylation and ethylation of ethylbenzene with ethanol were estimated by non-linear regression analysis. The apparent activation energy of benzene ethylation (E_1) was found to be higher than the value for ethylbenzene ethylation (E_2). In addition, the effect of feed ratio (B/E) on the activation energies and products distribution was also investigated in this study.

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1. Introduction

Ethylbenzene (EB) is an important raw material in the petrochemical industry for the manufacture of styrene, which is a widely used industrial monomer. Styrene is an important monomer in the production of synthetic rubber, synthetic plastics and resins. Ethylbenzene has a limited use also as a solvent and for the production of dyes [1]. The ethylbenzene production in 2010 is estimated to be about 34 million metric tons [2]. Conventionally, ethylbenzene is produced by benzene alkylation with ethylene using homogeneous mineral acids such as aluminium chloride or phosphoric acid as catalysts that cause a number of problems concerning handling, safety, corrosion and waste disposal [3,4]. Benzene ethylation over zeolite based catalyst to produce ethylbenzene amongst other product is gaining remarkable attention and has been replacing the convectional catalysts. The vapour phase alkylation of benzene with ethanol in the presence of ZSM-5 zeolites is the famous Mobil–Badger process, which is now in commercial practice for production of ethylbenzene [5].

Lately, the direct use of ethanol, instead of ethene, as an alkylating agent with benzene for this reaction has gained more attention [6–8]. A long stable catalyst life is observed when alcohol, rather than ethylene, is used as an alkylating agent [1]. In addition to the academic interest, the direct use of ethanol in manufacture of ethylbenzene is also economical significance to those countries and regions where biomass derived alcohol is an additional raw material for the manufacture of chemicals. The use of zeolite catalysts offers an environmentally friendly route to ethylbenzene and the possibility of achieving superior product selectivity through pore size control [9–12]. Zeolites are attractive materials for alkylation reactions because of their acid–base properties. The role of the acid–base properties of zeolites catalysts on product distribution of aromatic alkylation reactions has been reviewed by Giordano et al. [13]. The ring-alkylation mechanism over acid catalysts would proceed via the formation of methoxonium ion, which requires Bronsted acid sites [14–18]. Chandawar et al. [19] reported a significant improvement in ethylbenzene selectivity by modification of ZSM-5 by P or B to eliminate the strong acid sites on the surface of the catalyst. Levesque and Dao [20] also studied the alkylation of benzene with ethanol using steamed-treated ZSM-5 zeolite and chryso-zeolite ZSM-5 catalysts. They reported that ethylbenzene selectivity increased at high benzene/ethanol molar ratio. Gao et al. [21] studied the effect of zinc salt on the synthesis of ZSM-5 for alkylation of benzene with ethanol. They observed that the increase in ethylbenzene selectivity was due to higher Lewis/Bronsted acid ratio and the smaller crystal size. Ethylation

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of benzene with ethanol over MnAPO-5 catalyst was also studied by Raj et al. [22]. Raj et al. [22] used a molar ratio of 1:1 (benzene/ethanol) and obtained a significant amount of ethylbenzene at 400 °C.

In addition to catalyst development and study of reaction mechanism, the kinetics of benzene ethylation has been studied over different zeolites types. One of the earliest kinetic models proposed for this reaction was that due to Sridevi et al. [5]. Different models based on Langmuir–Hinshelwood–Hougen–Watson reaction mechanisms were proposed and a mathematical fit for the best model was found. They determined the activation energy of benzene ethylation to be ~60.03 kJ/mol over AlCl$_3$-impregnated 13X zeolite catalyst at constant benzene to ethanol molar ratio of 3:1. Similarly, kinetic model for benzene alkylation over cerium exchanged NaX zeolite catalyst was also studied by Barman et al. [1]. They reported an apparent energy of activation of ~56 kJ/mol for the alkylation reaction at constant benzene to ethanol molar ratio of 3:1. In most of the kinetic studies mentioned above, ethylbenzene is usually considered to be the only product of the alkylation reaction, while other products like diethylbenzene (DEB) are negligible, whereas, the present study took into consideration the second alkylation step in its kinetic model development. Moreover, virtually all of these studies were carried out in fixed-bed reactors where temperature and concentration gradients may have significant effects on the values of estimated model parameters, as pointed out by Ma and Savage [23]. Furthermore, in most of the previous kinetic studies on benzene ethylation, the deactivation of catalyst was not adequately accounted for, in the development of the kinetic models used in such studies.

The present study is aimed at investigating the ethylation of benzene with ethanol over fresh and precoked ZSM-5 based catalyst in a riser simulator in which temperature and concentration gradients are almost eliminated because of intense mixing. The study will focus on the effect of reaction conditions (time, temperature, and conversion) on ethylbenzene yield, DEB yield, p-DEB to o-DEB (P/O) ratio, and EB to DEB ratio. In addition, the effect of varying the reactants feed molar ratio on the activation energies and products distribution was also investigated in this study. A comprehensive kinetic modeling of the reaction, which will account for all the important reaction steps including the formation of diethylbenzene, will also be carried out.

2. Experimental

2.1. The riser simulator

All the experimental runs were carried out in a 45 cm^3 riser simulator (see Fig. 1). This reactor is novel bench-scale equipment with an internal recycle unit invented by de Lasa [24]. The riser simulator consists of two outer shells, the lower section and the upper section, which allow to load or to unload the catalyst 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 shell. A metallic gasket seals the two chambers with an impeller located in the upper section. A packing gland assembly and a cooling jacket surrounding the shaft provide support for the impeller. Upon rotation of the shaft, gas is forced outward from the centre of the impeller towards the walls. This creates a lower pressure in the centre region of the impeller thus inducing flow of gas upward through the catalyst chamber from the bottom of the reactor annular region where the pressure is slightly higher. The impeller provides a fluidized-bed of catalyst particles as well as intense gas mixing inside the reactor. The riser simulator consists of two omega CN9000 series temperature controllers that control the vacuum box and reactor temperature. These controllers
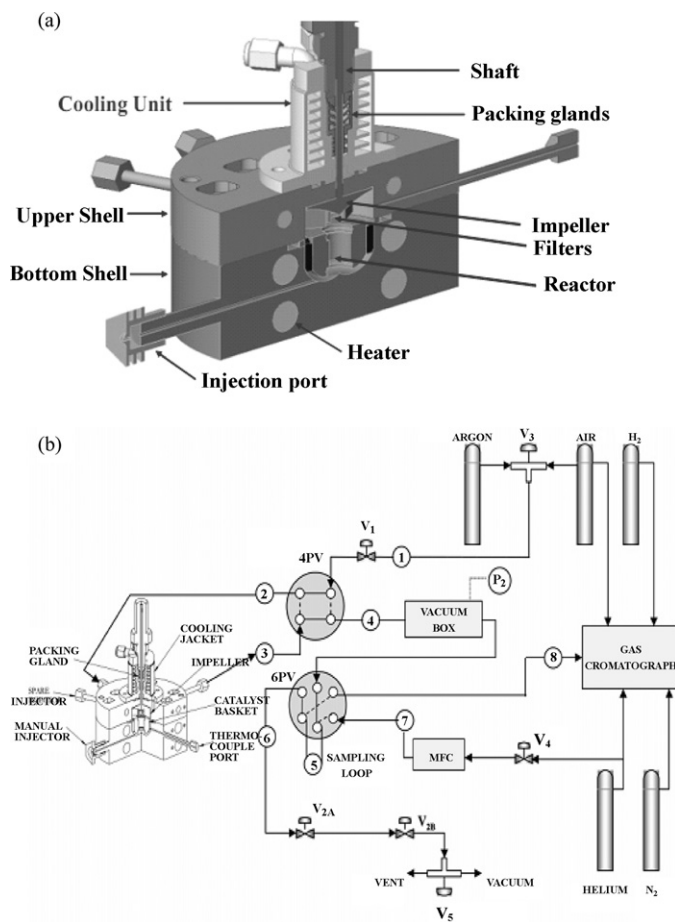

Fig. 1. (a) Schematic diagram of the riser simulator and (b) schematic diagram of the riser simulator experimental set-up.

are calibrated to work with K-type omega thermocouples. One of the thermocouple is connected to catalyst basket, from where the temperature in the reactor is measured as shown in Fig. 1.

The riser simulator operates in conjunction with series of sampling valves that allow for injection of the feedstock and withdrawal of reaction products in short periods of time, as shown in Fig. 1b. A four-port valve enables the connection and isolation of the 45 cm^3 reactor and the vacuum box, and a six-port valve allows for the collection of a sample of reaction products in a sampling loop. Vacuum box and reactor pressure are displayed on two Omega DP series pressure displays. The pressures are displayed in pounds per square inch absolute (psia). These displays are calibrated for use with Omega pressure transducers, rated for 50 psia maximum pressure. During the change of state from liquid (feedstock) to gaseous state, the pressure was noticed to increase from ~14.7 to 38 psi. Thereafter, an insignificant change in pressure was noticed after reactant vapourization. This is due to fact that alkylation reaction was dominant in this reaction as compared to cracking reaction. Gas mixing patterns in a riser simulator represent a well-mixed unit. Ginsburg et al. [25] reported that gas mixing times corresponding to high recirculation rates in this unit occur over impeller rotational speeds ranging from 3000 to 6000 rpm and total reactor pressures ranging from 1 to 5 atm. Well-mixed conditions, in the riser simulator, were reported by Pekediz [26], for a 7800-rpm shaft rotation. A detailed description of various riser simulator components, sequence of injection and sampling can be found in Kraemer [27].

Table 1
Catalyst characterization.

Catalyst	Surface area (m²/g)	Na₂O (%)	Acidity (mmol/g)	Weak acid site (%)	Strong acid site (%)
Fresh	70	Negligible	0.23	62.5	37.5
Precoked	63	Negligible	0.18	66.67	33.33

2.2. Materials

2.2.1. Catalyst preparation/characterization

The ZSM-5 zeolite used in this work was obtained from Tosoh Company, Japan. The as-synthesized Na zeolite was ion-exchanged with NH_4NO_3 to replace the Na cation with NH_4^+. Following this, NH_3 was removed and the H form of the zeolite was spray dried using kaolin and alumina as the filler and a silica sol as the binder. Laser scattering particle size analyzer was used to determine the size of the catalyst particle. The resulting 60 μm catalyst particles had the following composition: 30 wt% zeolite, 50 wt% kaolin and alumina, and 20 wt% silica sol. The process of Na removal was repeated for the pelletized catalyst. Following this, the catalyst was calcined at 600 °C for 2 h. The total acidity was determined using NH_3 desorption method. The precoked catalyst was prepared by treating 800 mg of fresh catalyst with 100 μL of carbonaceous 1,3,5-TIPB under mild reaction conditions (temperature 400 °C, reaction of 3 s). 1,3,5-TIPB was used because its kinetic diameter is larger than the pore opening of ZSM-5, thereby restricting coke deposit to the external surface of the catalyst only. The catalytic cracking of 1,3,5-TIPB was carried out in the riser simulator at 400 °C for 3 s. Less than 10% conversion was obtained at this reaction condition, with less than 3% propylene as product.

Koch and Reschetilowski [28] used 1,3,5-TIPB as a model feed in hydrocarbon cracking over Y-zeolite and they found out that, due the kinetic diameter of 1,3,5-TIPB (0.94 nm) there was geometrical restrictions to the inner centers of zeolite Y. Comparing Y-zeolite to ZSM-5 with a smaller pore size, more restriction is expected over this catalyst. Furthermore, Zhang et al. [29] carried out the catalytic cracking of 1,3,5-TIPB over ZSM-5 and a very low conversion was obtained. They attributed these to the limited pore size of ZSM-5, because most of the active sites of ZSM-5 could not be fully contacted and the catalytic cracking is only processed on the surface of the catalyst. Hence, the internal active sites were not affected significantly by precoking. The total acidities and their distribution along with the measured Brunauer–Emmett–Teller (BET) surface areas for both the fresh and the precoked catalyst are summarized in Table 1, while Fig. 2 shows a comparison between the acidities of fresh and precoked catalyst. All chemicals used in this work were obtained from Sigma–Aldrich.

2.2.2. Feedstock

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

2.3. Procedure

2.3.1. Fresh catalyst

Catalytic experiments were carried out in the riser simulator with a feed mixture of benzene and ethanol for residence times of 3, 5, 7, 10, 13, and 15 s at temperatures of 300, 325, 350 and 400 °C. About 800 mg of the 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 to a pressure of ~0.5 psi to prevent any condensation of hydrocarbons inside the box. The heating of the riser simulator

was conducted under continuous flow of inert gas (Ar), and it 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 Ar. The temperature controller was set to the desired reaction temperature, and in the same manner, the timer was adjusted to the desired reaction time. At this point, the GC is started and set to the desired conditions. Once the reactor and the gas chromatograph have reached the desired operating conditions, 0.162 g of the feedstock was injected directly into the reactor via a loaded syringe. After the reaction, the four-port valve opens immediately, ensuring that the reaction was terminated and the entire product stream was sent on-line to analytical equipment via a preheated vacuum box chamber. The products were analyzed in an Agilent 6890N gas chromatograph with a flame ionization detector and a capillary column INNOWAX, 60-m cross-linked methyl silicone with an internal diameter of 0.32 mm.

The amount of coke deposited on the spent catalysts was determined by a common combustion method. In this method, a carbon analyzer multi EA 2000 (Analytikjena) is used. Oxygen is supplied to the unit directly. The multi EA 2000 with CS Module is a specially developed system to permit simultaneous or separate determination of the total carbon and total sulphur in samples of solids, pastes and liquids by means of high temperature oxidation in a current of oxygen. It is based on special high temperature ceramics (HTC) technology which renders a catalyst superfluous. By combining the finely tuned non-dispersive infrared gas analysis (NDIR) detection which is selective to CO_2/SO_2 with the patented Verweilzeitgekoppelte Integration fur TOC-Analysen (VITA) procedure, which takes into account the dwelling time, the analysis possible is very precise.

The aliquot of the sample is accurately weighed into the combustion boat and delivered complete into the hot zone of the furnace. There, pyrolysis and oxidation of the sample occurs at a high temperature in the stream of oxygen ($R + O_2 \rightarrow CO_2 + H_2O$, where R is a substance with carbon content). The gas produced in the pyrolysis is drawn through a glass tube filled with a specialist desiccant. This desiccation tube also serves as a particle filter, so
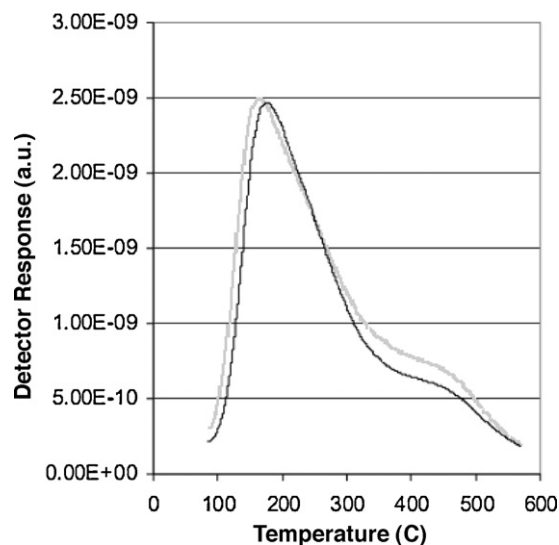

Fig. 2. Comparison between the acidities of fresh (. . .) and precoked (—) catalyst.

that no water or dust can get into the detection system of the device. An NDIR detector is used to determine the CO_2 content in the carrier gas. Gases whose molecules are composed of different types of atom possess specific absorption bands in the infrared wavelength range. The concentration of CO_2 is signaled several times per second. An integral over time is created from the series of signals. The integral is proportional to the concentration of carbon in the sample analyzed. A calibration function is then used to calculate the amount of carbon in the sample. The calibrations allows for any changes to flow arising over time because of such factors as the ageing process, dirt getting into flow regulators, or the desiccants going lumpy, will not automatically necessitate recalibration, which is a positive factor reducing the frequency of desiccant replacement. A small amount of the spent catalyst (0.35 g) is used for the analysis. During the course of the investigation, a number of runs were repeated to check for reproducibility in the experimental results, which were found to be excellent. Typical errors were in the range of ±2%.

2.3.2. Precoked catalyst

Coke is selectively deposited on the external surface of zeolites in order to cover the external active sites which are responsible for undesirable secondary reactions. Generally, molecules with large kinetic diameters which cannot penetrate into zeolite pores are used thereby limiting the reaction of these compounds to the external surface of the zeolite. Hence, coke formed is essentially deposited on the catalyst external surface. Precoking using carbonaceous compounds with large molecules has been reported in the literature [30,31]. Since coke is deposited only externally, it is assumed that the internal sites stay essentially unchanged. Therefore, although precoking generally reduces the total number of acid sites, it keeps enough acid sites to catalyze the reaction [30,31]. Catalyst precoking has been observed to have a significant effect on para-selectivity. The significant increase in para-selectivity after precoking is attributed to the partial deactivation of the external active sites where p-isomers (generated inside ZSM-5 pores) undergo disproportionation reaction. Consequently, this leads to an increase in the rate of formation of p-isomers, while the rate of disproportionation reaction is significantly decreased.

In the experimental runs with the precoked catalyst, 100 μL of 1,3,5-TIPB was injected at 400 °C into the reactor after loading the reactor basket with 800 mg of fresh catalyst, and a limited reaction was allowed to take place for only 3 s. The amount of coke deposited on the catalyst from 1,3,5-TIPB was found to be 0.15 wt%. The system was then purged and cleaned with argon for 30 min.

Regarding the nature of coke deposited, different analytical techniques have been used in the literature to characterize the coke formed over different zeolite catalyst at different temperatures. One of those methods is the one developed by Guisnet and Magnoux [32] in which the coked catalyst is treated with HF solution and the soluble coke which dissolve in CH_2Cl_2, is analyzed through GC–MS coupling. Similar approach developed by Guisnet and Magnoux [32] describe above, was used to determine the developed formula for the components soluble in CH_2Cl_2 and was analyzed by an Agilent GC–MS (GC 6890N-MD 5973N) with a DB5-MS column (30 m × 0.25 mm). The column program is: injector temperature, 250 °C; initial column temperature, 40 °C; initial time, 5 min; heating rate, 12 °C/min; final temperature, 320 °C; final time, 25 min; carrier gas, He, 1 mL/min; average velocity, 38 cm/s; solvent delay, 6 min. An alkyl benzene (methyl benzene) compounds were identified as the coke component over the precoked catalyst.

According to Guisnet and Magnoux [33], the H/C atomic ratio can be considered as a measurement of the aromaticity of the coke. The elemental analyzer (Model Vario EL) was also used to quantify the polyaromatic character of the coke over the precoked catalyst, by measuring the H/C atomic ratio. By applying this technique,
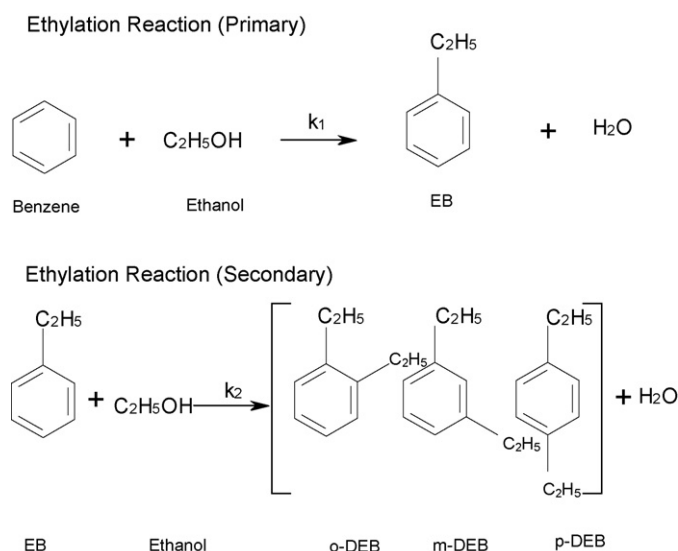

Fig. 3. Primary and secondary reactions occurring during ethylation of benzene with ethanol.

any water released from the catalyst itself could interfere with the result, giving higher hydrogen (H) value [34]. To overcome this problem, water was quantified accurately in the catalyst sample by Karl Fischer titration. A Karl Fischer coulometer (Model Mettler DL 37) was used for water determination. Then, the hydrogen in water was subtracted from the total amount of H of the catalyst sample measured by elemental analyzer. The corrected H value is used in calculating the H/C ratio. The hydrogen to carbon ratio of the coke content over the precoked catalyst was found to be ~1.6.

It is of paramount importance to note that, the hydrogen to carbon atomic ratio as well as the obtained developed formula for the coke noticed from the coke over the precoked catalyst was not used in any section of this study; rather, the carbonaceous compound was just used to cover part of external active sites which are responsible for undesirable secondary reactions (Fig. 3).

3. Results and discussion

3.1. Benzene conversion

The main products of the ethylation reaction of benzene with ethanol over ZSM-5 based catalyst were found to be ethylbenzene and diethylbenzene. Negligible amounts of toluene, m-xylene and gaseous hydrocarbons were also detected. The experimental results showed that the conversion occurred via ethylation only. It was observed that, in spite of the short reaction times (3–15 s), reasonable benzene conversions were obtained. The product distribution is reproduced in Table 2. Fig. 4 shows the variation of benzene conversion with reaction time and temperature for the fresh catalyst based on time on stream. It is evident from this figure that benzene conversion increased with both reaction time and temperature, reaching a maximum of ~17% at 400 °C for a reaction time of 15 s. For all the reaction temperatures, it was observed that conversion increased by ~4–5.33 times when reaction time was increased from 3 to 15 s. Similarly, for all reaction times, benzene conversion was also found to increase as temperature was increased from 300 to 400 °C. This is in an agreement with observation made by Levesque and Dao [20] during the alkylation of benzene with aqueous ethanol solution over steamed-treated ZSM-5 and chryso-zeolite ZMS-5 catalysts. They reported that benzene conversion increased regularly with temperature to reach a maximum in the region of 725 K. A possible reaction scheme to represent the observed product dis-

Table 2
Product distribution of benzene ethylation over (a) the fresh catalyst and (b) the precoked catalyst at 400 and 350 °C, benzene/ethanol ratio = 1:1.

| Temperaure (°C)	Time (s)	Yield (%)							Benzene conversion (%)	P/O
		BZ	Ethanol	EB	m-DEB	p-DEB	o-DEB	Total DEB		
(a) Fresh catalyst										
400	5	58.60	30.06	5.15	0.42	0.45	0.14	1.12	6.84	3.21
	10	55.53	25.19	8.13	1.45	1.61	0.19	3.24	11.72	8.47
	15	52.24	21.07	10.24	2.91	3.04	0.39	6.34	16.95	7.79
350	5	60.07	32.07	3.41	0.30	0.41	0.04	0.75	4.50	10.25
	10	57.24	26.53	6.31	0.75	1.34	0.09	2.17	8.99	14.89
	15	55.00	20.99	7.22	1.76	2.38	0.19	4.33	12.56	12.53
(b) Precoked catalyst										
400	5	60.25	28.90	2.73	0.52	0.81	0.06	1.38	4.21	13.50
	10	57.10	24.58	5.84	1.23	1.92	0.12	3.27	9.22	16.00
	15	53.81	21.31	8.64	2.37	2.97	0.19	5.53	14.45	15.63
350	5	61.27	30.82	1.60	0.34	0.53	0.03	0.91	2.56	17.67
	10	58.62	26.34	4.18	0.96	1.54	0.09	2.60	6.80	17.11
	15	56.33	22.87	6.31	1.46	2.46	0.14	4.01	10.44	17.57
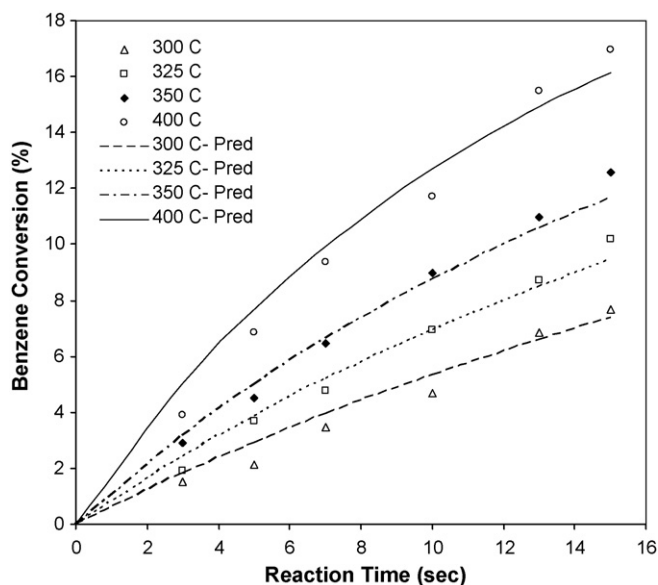
Fig. 4. Effect of reaction conditions on benzene conversion.

tribution is shown in Scheme 1. The primary reaction pathway is ethylation of benzene with ethanol to produce ethylbenzene and water. The formation of DEB from the ethylation of ethylbenzene with ethanol represents the secondary reaction.

Benzene conversion was also observed over the precoked catalyst and it showed a similar dependence on temperature and reaction time as with the fresh catalyst, however, the values were slightly lower than those obtained over the fresh catalyst. Fig. 5 compares benzene conversion over the fresh and precoked catalyst at temperatures of 350 and 400 °C for reaction times of 5, 10, and 15 s. From Fig. 5, it can be seen that, at both 350 and 400 °C and a reaction time of 10 s, less than 25% decrease was noticed in the benzene conversion between the fresh and precoked catalyst. However, conversion reduces to less than 17% at a reaction time of 15 s, for both 350 and 400 °C. The mild effect of catalyst precoking on benzene conversion is an indication that coke deposit was

restricted to the external surface of the catalyst without interfering much with the acid sites within the pores of the catalyst where alkylation largely takes place. The slight reduction in benzene conversion can be linked to the reduction of the total number of active sites due to partial deactivation and also due to problems of benzene diffusion, which may occur as a result of a possible blockage of some of the pore openings of the catalyst by the relatively larger molecules of 1,3,5-TIBP. The effect of benzene conversion on ethylbenzene and diethylbenzene selectivity at 400 °C is given in Fig. 6. Diethylbenzene shows a high dependence on benzene conversion and was noticed to increase as benzene conversion increases. Ethylbenzene on the other hand, also shows a high dependence on benzene conversion, but was observed to decrease as benzene conversion increases.

3.2. Effect of feed mole ratio

The effect of feed mole ratios (benzene to ethanol) on benzene conversion, product selectivity and energies of activation were investigated over ZSM-5 based catalyst. Effect of benzene to ethanol mole ratio in the feed mixture on benzene conversion was studied by varying the ratio from 1:1 to 3:1 at 400 °C, for reaction times of 5, 10 and 15 s. Table 3 presents the results of product selectivity over ZSM-5 based catalyst in the ethylation of benzene with
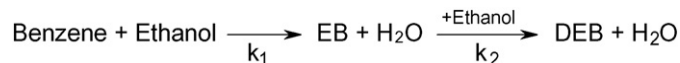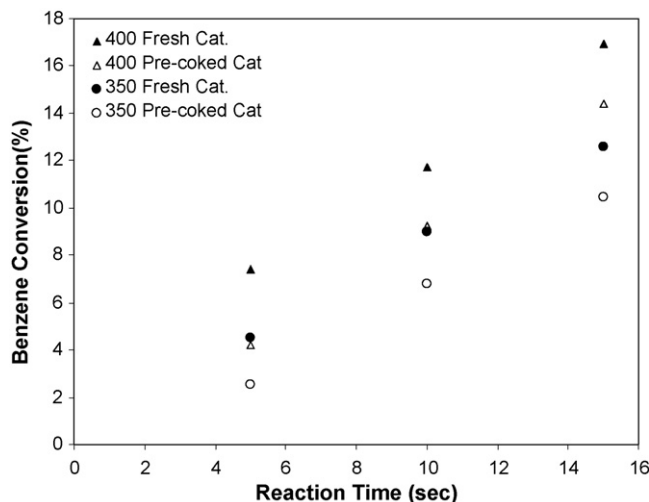

Scheme 1.

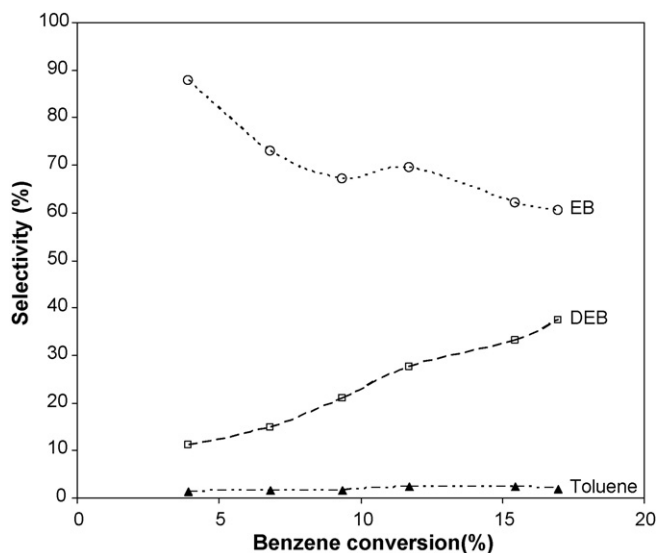**Fig. 5.** Comparison of benzene conversions for fresh and precoked catalyst.

Fig. 6. Effect of benzene conversion on products selectivity.

Fig. 7. Effect of feed mole ratio (benzene to ethanol) on benzene conversion at 400 °C.

ethanol with different feed mole ratios. The conversion of benzene shows a significant decline with increasing feed mole ratio of benzene to ethanol from 1:1 to 3:1. The results are shown in Fig. 7. This is because most of the active sites of the catalyst surface were blocked by a large excess of aromatic reactant injected into the system. An increased dilution of ethanol by benzene, also account for the reduction in conversion. With increasing feed mole ratios of benzene to ethanol, the opportunity of benzene attacked by ethyl cations are reduced, and then a lower benzene conversion is obtained. This is in agreement with the findings of Levesque and Dao [20], in which the author reported similar drop for conversion of benzene over steamed-treated ZSM-5 zeolite catalyst. With an increase in the ratio of benzene to ethanol, the selectivity for ethylbenzene is improved at the expense of diethylbenzene. About ~44% increase in the selectivity of EB was noticed by increasing the feed mole ratio from 1:1 to 3:1 at 400 °C, for a reaction time of 15 s. On other hand, selectivity of DEB decreased from ~37.40 to 9.17, representing a 75% decrease. The observed trend in the selectivity of the EB and DEB is consistent with the work of Levesque and Dao [20] during the alkylation of benzene over steamed-treated ZSM-5 zeolite and chryso-zeolite ZSM-5 based catalyst. The increase of feed mole ratios (benzene/ethanol) results in an increase of the primary alkylation and decrease of the secondary alkylation reaction.

3.3. Ethylbenzene yield and EB/DEB yield

As shown in Fig. 8, ethylbenzene yield, similarly to benzene conversion, increased with both reaction time and temperature over the fresh catalyst. A maximum yield of ~10.24% was achieved at 400 °C at 16.95% benzene conversion. This corresponds to an ethylbenzene selectivity of ~60.41%. Similarly, Fig. 9 shows diethylbenzene yield with reaction time and temperature over the fresh catalyst. From the figure, it is observed that diethylbenzene yield increased with both reaction time and temperature over the fresh catalyst. The highest diethylbenzene yield of ~6.34% was achieved at 400 °C at 16.95% benzene conversion, corresponding to a diethylbenzene selectivity of ~37.40%. Fig. 10 shows the variation of the ratio of ethylbenzene yield to the yield of diethylbenzene with temperature for a reaction time of 15 s. It is observed from the figure that, as temperature was increased from 300 to 400 °C, the ratio of ethylbenzene yield to that of DEB decreased constantly, indi-

Table 3
Effect of feed ratio on products selectivity over ZSM-5.

Performance	Feed ratio (benzene:ethanol)		
	1:1	2:1	3:1
Benzene conversion	16.95	16.45	9.67
Selectivity (wt%)			
Ethylbenzene	60.41	81.61	86.69
Diethylbenzene	37.40	15.53	9.17
Others	2.19	2.86	4.14
Diethylbenzene isomer (%)			
Para	47.95	44.62	47.64
Meta	45.89	48.50	45.42
Ortho	6.15	6.88	6.94

Temperature = 400 °C, reaction time = 15 s. Others: toluene, xylene and unidentified compounds.
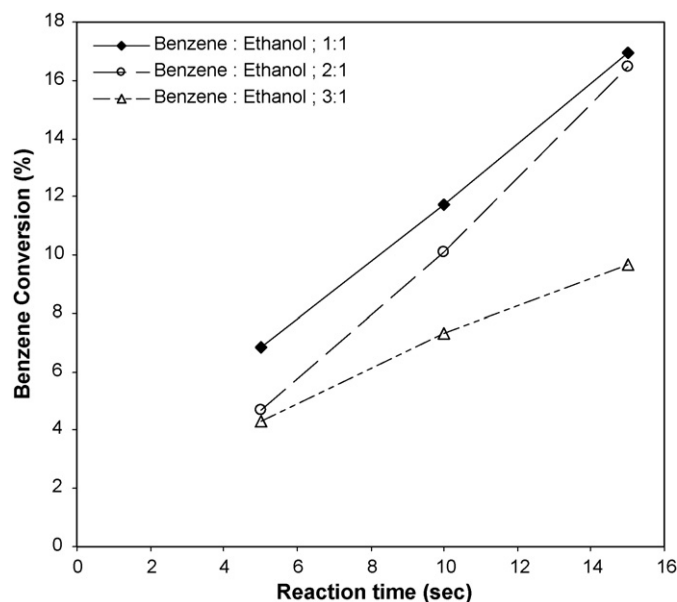

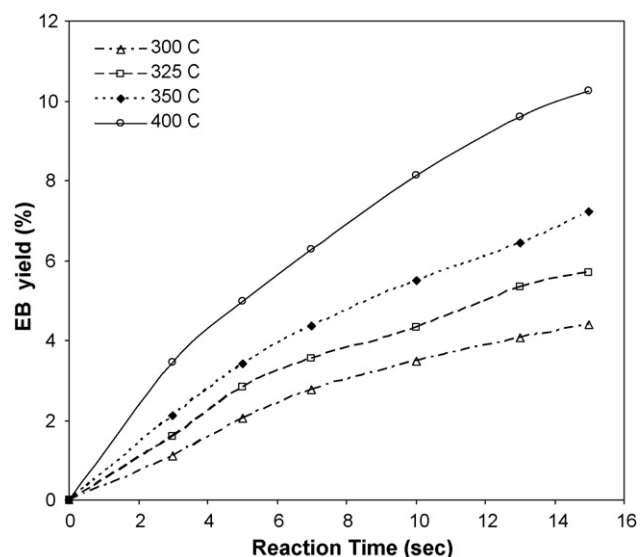**Fig. 8.** Variation of ethylbenzene yield with reaction conditions.
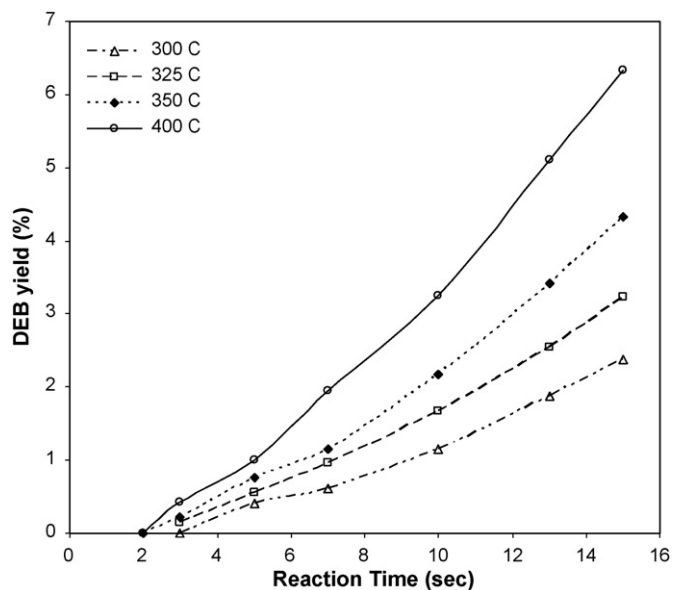
Fig. 9. Variation of diethylbenzene yield with reaction conditions.

Fig. 11. Variation of P/O with reaction time at different temperatures.

cating that the secondary ethylbenzene alkylation with ethanol to produce diethylbenzene is highly sensitive to temperature.

3.4. para-DEB/ortho-DEB (P/O) ratio

Table 3 shows the variation of the reaction products for para-, meta- and ortho-isomers. All the three isomers of diethylbenzene were detected in the GC analysis of the reaction product. However, the para-isomers were in higher proportion than the other isomers at all the conditions investigated in this study. Raj et al. [22], had reported that the critical diameter of p-isomer is smaller than meta, which implies that para-isomers diffuse out of the pores faster than the bulky meta-isomers, leading to greater para-selectivity. The ortho-isomer is not formed in significant amount in the ethylation reactions over ZMS-5 due to steric hindrance and low density of acid sites on external surface. Fig. 11 shows the variation of P/O ratios with reaction time at different temperatures. As can be seen from the figure, there is significant decrease in the P/O ratio as the temperature is increased. At 350 °C, P/O ratio
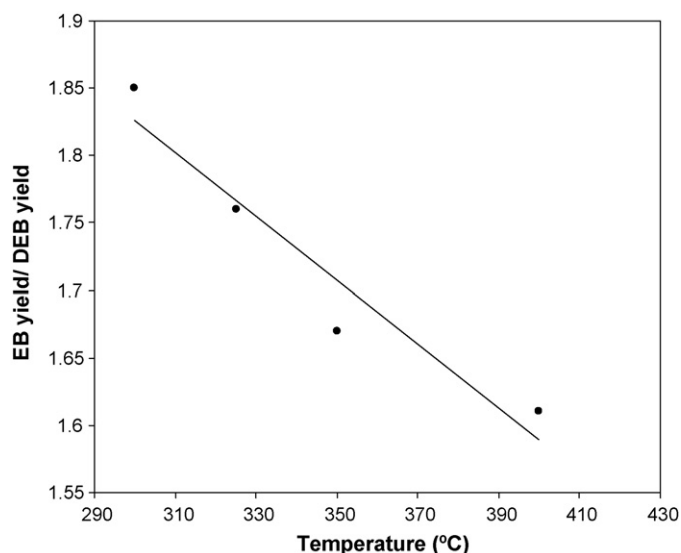

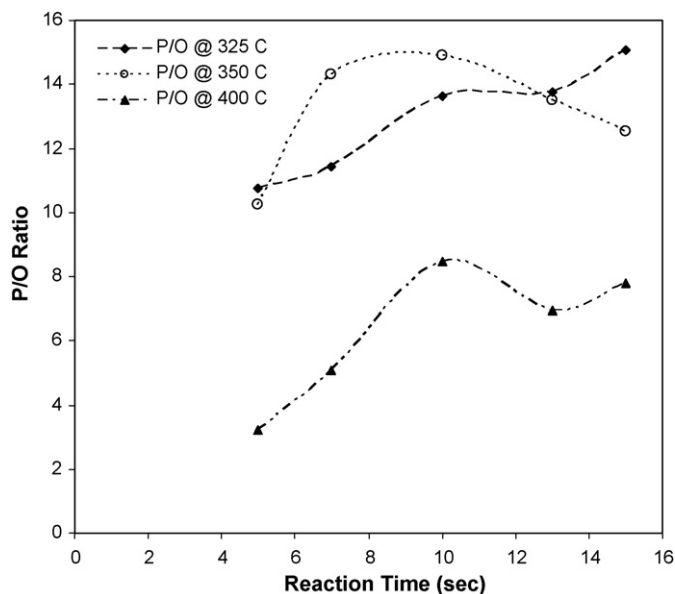Fig. 10. Variation of EB yield/diethylbenzene yield with temperature.

was found to increase with reaction time up to 10 s, but a sharp decrease in P/O ratio was noticed as the reaction time was further increased to 15 s. The observed decrease of P/O ratio as temperature was increased from 350 to 400 °C can be explained in terms of the effect of temperature on strength of adsorption of ethylbenzene and ethyl cation on the catalyst surface. The mechanism of the ethylation of ethylbenzene with ethanol was studied by Vijayaraghavan and Raj [7], they reported that the formation of p-DEB would require reaction between ethylbenzene in the vapour phase and ethyl cation on the catalyst surface while formation of m-DEB would require reaction between co-adsorbed ethylbenzene and ethyl cation on the catalyst surface. At lower temperature, most of the ethylbenzene is in the vapour state without much adsorption. Rajesh et al. [35] reported that when ethylbenzene in the vapour state approaches the layer of ethyl cations on the catalyst surface, it can better use its para-position for electrophilic attack to produce p-DEB, as its ortho-position offers little steric hindrance and the meta-position demand high activation energy for electrophilic attack.

It is well known that a post-synthesis modification of the HZSM-5, such as impregnation with coke deposition, can improve para-selectivity dramatically [36]. Catalyst precoking was observed to have a significant effect on the P/O ratio as presented in Table 2. This is due to the partial deactivation of the external active sites, which are responsible for the undesirable isomerization of the p-DEB formed in the pores of the catalyst into the other isomers. The ratio of p- to o-DEB (P/O) for the fresh and precoked catalyst at 350 and 400 °C for a benzene conversion of 10%, is presented in Fig. 12. It can be seen from this figure that, at 350 °C, the P/O ratio increased from ∼14.14 to ∼17.80, representing an increase of 26%. The effect of catalyst precoking became more visible at 400 °C, with P/O increasing from ∼6.80 to ∼16.12, representing a 137% increase. It is evident from this figure that, for all the reaction conditions studied, P/O was found to be much higher than the equilibrium value, which was reported by Halgeri [37] to be ∼1.875.

3.5. Coke content measurement

Cokes are mainly responsible for the deactivation of catalysts. The coke formation in zeolite has been widely studied [38] and
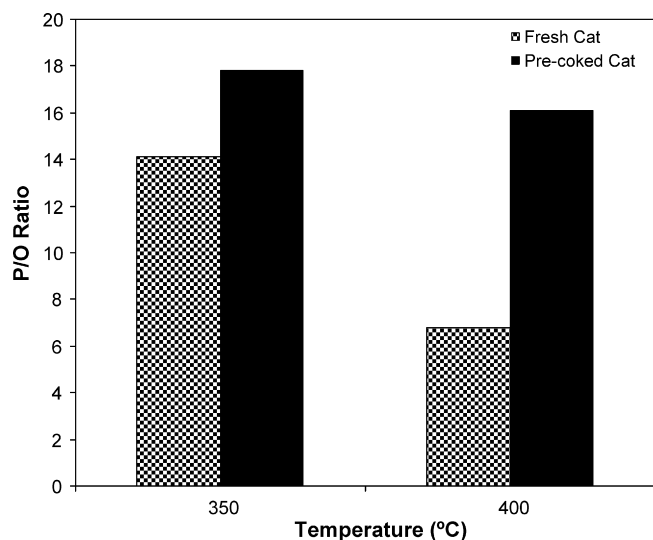
Fig. 12. Effect of catalyst precoking on P/O ratio.

depends on the size and shape of the space available near the active sites as well as the diffusion path of the organic molecules in the pores of zeolites. Coke was also measured at different conditions. Table 4 reveals the amount of coke deposition. It is clear that the ratio of coke weight percent to percent conversion is very small, ranging from 0.015 and 0.028 at all reaction conditions. This implies that the ethylation of benzene with ethanol over ZSM-5 based catalyst is not accompanied by appreciable coke deposition.

4. Kinetic modeling

4.1. Model development

The experimental results were modeled using catalyst deactivation function based on two different models. One of the catalyst activity decay model was based on time on stream (TOS), while the other was based on reactant conversion (RC) model.

4.1.1. Catalyst activity decay function based on time on stream (TOS)

The catalyst activity decay model based on time on stream was initially suggested by Voorhies [39]. This model, the so-called "time on stream" model (TOS) was also successfully tested, for the ethylation of ethylbenzene with ethanol [40]. To develop a suitable kinetic model representing the overall ethylation of benzene, the reaction network shown in Scheme 1 is used. The following set of species balances and catalytic reactions can be written:

Table 4
Coke formation for benzene ethylation with ethanol at different reaction conditions.

Temperature (°C)/time (s)	Conv (%)	Coke (wt%)	Coke/conv
350			
5	4.50	0.127	0.028
10	8.99	0.150	0.017
15	12.56	0.227	0.018
400			
5	6.84	0.149	0.022
10	11.72	0.213	0.018
15	16.95	0.247	0.015

Benzene/ethanol ratio = 1:1.

Rate of disappearance of benzene:

$$-\frac{V}{W_c}\frac{dC_{BZ}}{dt} = \eta k_1 C_{BZ} C_E \ \exp(-\alpha t) \tag{1}$$

Rate of formation of ethylbenzene:

$$\frac{V}{W_c}\frac{dC_{EB}}{dt} = (\eta k_1 C_{BZ} C_E - \eta k_2 C_{EB} C_E)\exp(-\alpha t) \tag{2}$$

Rate of formation of diethyl benzene:

$$\frac{V}{W_c}\frac{dC_{DEB}}{dt} = \eta k_2 C_{EB} C_E \ \exp(-\alpha t) \tag{3}$$

The measurable variables from our chromatographic analysis are the weight fraction of the species, y_x, in the system. By definition the molar concentration, c_x of every species in the system can be related to its mass fraction, y_x by the following relation:

$$c_x = \frac{y_x W_{hc}}{V \ MW_x} \tag{4}$$

where W_{hc} is the weight of feedstock injected into the reactor, MW_x is the molecular weight of specie x in the system, V is the volume of riser simulator, t = time, α = catalyst decay constant and η = an effectiveness factor to account for the diffusion of benzene and ethanol into the pores of the catalyst. Benzene and ethylbenzene have almost the same critical molecular diameter, therefore a single effectiveness factor was considered for them. Substituting Eq. (4) into Eqs. (1)–(3), we have the following first-order differential equations which are in terms of weight fractions of the species:

$$\frac{dy_{BZ}}{dt} = -\eta B_1 k_1 y_{BZ} y_E \frac{W_c}{V} \ \exp(-\alpha t) \tag{5}$$

$$\frac{dy_{EB}}{dt} = [\eta B_2 k_1 y_{BZ} y_E - \eta B_1 k_2 y_{EB} y_E] \frac{W_c}{V} \ \exp(-\alpha t) \tag{6}$$

$$\frac{dy_{DEB}}{dt} = \eta B_3 k_2 y_{EB} y_E \frac{W_c}{V} \ \exp(-\alpha t) \tag{7}$$

B_1, B_2 and B_3 are lumped constants given below:

$$B_1 = \frac{W_{hc}}{V \ MW_E} \tag{8}$$

$$B_2 = \frac{MW_{EB} W_{hc}}{V MW_{BZ} MW_E} \tag{9}$$

$$B_3 = \frac{MW_{DEB} W_{hc}}{V MW_{EB} MW_E} \tag{10}$$

Eqs. (5)–(7) contain five parameters, k_1, k_2, E_1, E_2, and α, which are to be determined by fitting into experimental data.

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

$$k_i = k_{0i} \exp\left[\frac{-E_i}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{11}$$

Since the experimental runs were done at 300, 325, 350 and 400 °C, T_0 was calculated to be 343.75 °C.

Where T_0 is an average temperature introduced to reduce parameter interaction [41], k_{0i} is the rate constant for reaction i at T_0, W_c is the weight of catalyst and E_i is the activation energy for reaction i.

The above proposed model equations were based on the following simplifying assumptions:

(1) The ethylation of benzene for both molar ratios of benzene to ethanol (1:1 and 2:1), follows simple second-order kinetics. A

third order kinetics was found not suitable for the 2:1 (benzene/ethanol) molar ratio.

(2) Catalysts deactivation is assumed to be a function of time on stream (TOS). And a single deactivation function was defined for all the reactions.

(3) Ethylation reactions were all assumed to occur via an irreversible reaction path. A similar assumption has been made by previous workers in the area [1,5].

(4) Isothermal operating conditions can also be assumed given the design of the riser simulator unit and the relatively small amount of reacting species [24]. This is justified by the negligible temperature change observed during the reactions.

(5) A pseudo-first-order reaction kinetic for all species involved in the reactions.

(6) Negligible thermal conversion.

(7) Since, benzene and ethylbenzene have almost the same critical molecular diameter, a single effectiveness factor was considered for them.

(8) The effectiveness factor η was taken to be unity. This is justified by the fact that p-xylene formed by catalytic reaction can easily escape via the pores of ZSM-5 [42], comparing benzene and ethylbenzene with almost the same critical diameter as p-xylene; negligible diffusion limitation is also expected in this reaction.

4.1.2. Catalyst activity decay function based on reactant conversion (RC)

The catalyst activity decay function can be conveniently expressed as a function of reactant converted. This meaningful deactivation function (reactant conversion model) was proposed by de Lasa [43]. The following set of species balances and catalytic reactions can be written based on the reaction network shown in Scheme 1:

Rate of disappearance of benzene:

$$-\frac{V}{W_c}\frac{dC_{BZ}}{dt} = \eta k_1 C_{BZ} C_E \varphi \tag{12}$$

Rate of formation of ethylbenzene:

$$\frac{V}{W_c}\frac{dC_{EB}}{dt} = (\eta k_1 C_{BZ} C_E - \eta k_2 C_{EB} C_E)\varphi \tag{13}$$

Rate of formation of diethyl benzene:

$$\frac{V}{W_c}\frac{dC_{DEB}}{dt} = \eta k_2 C_{EB} C_E \varphi \tag{14}$$

where η is the effectiveness factor and $\varphi = \exp(-\lambda(1 - y_{BZ}))$ represents catalyst deactivation based on reactant converted (RC) model proposed by de Lasa [43]. This type of model has been reported to incorporate a sound mechanistic description of catalyst deactivation [44], and also allows for changes of chemical species without extra requirement of measuring the coke concentration [43]:

$$k_i = k_{0i} \exp\left[\frac{-E_i}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{15}$$

where T_0 is the average reaction temperature introduced for re-parameterization of kinetic constants [41]:

Substituting Eq. (4) into Eqs. (12)–(14), we have the following first-order differential equations which are in terms of weight fractions of the species:

$$\frac{dy_{BZ}}{dt} = -\eta B_1 k_1 y_{BZ} y_E \frac{W_c}{V} \exp(-\lambda(1 - y_{BZ})) \tag{16}$$

$$\frac{dy_{EB}}{dt} = [\eta B_2 k_1 y_{BZ} y_E - \eta B_1 k_2 y_{EB} y_E] \frac{W_c}{V} \exp(-\lambda(1 - y_{BZ})) \tag{17}$$

Table 5
Estimated kinetic parameters based on time on stream (TOS model). Feed ratio = 1:1 (benzene:ethanol).

Parameters	Values			
	k_1	k_2	α (1/s)	r^2
E_i (kJ/mol)	34.69	9.53	0.0250	0.99
95% CL	0.59	1.43	0.0035	
$k_{0i}{}^{a} \times 10^4$ [m³/(kg of catalyst s)]	0.170	1.118		
95% CL $\times 10^4$	0.004	0.033		

[a] Pre-exponential factor as obtained from Eq. (8); unit for second-order (m⁶/kg of catalyst s).

Table 6
Estimated kinetic parameters based on time on stream (TOS model). Feed ratio = 2:1 (benzene:ethanol).

Parameters	Values			
	k_1	k_2	α (1/s)	r^2
E_i (kJ/mol)	29.95	11.03	0.0925	0.99
95% CL	2.71	8.62	0.0146	
$k_{0i}{}^{a} \times 10^4$ [m³/(kg of catalyst s)]	0.153	0.627		
95% CL $\times 10^4$	0.018	0.099		

[a] Pre-exponential factor as obtained from Eq. (8); unit for second-order (m⁶/kg of catalyst s).

Table 7
Correlation matrix for benzene ethylation (TOS model) (feed ratio = 1:1 (benzene:ethanol)).

	k_1	E_1	α
k_1	1.0000	−0.2205	0.9461
E_1	−0.2205	1.0000	−0.1230
α	0.9461	−0.1230	1.0000

$$\frac{dy_{DEB}}{dt} = \eta B_3 k_2 y_{EB} y_E \frac{W_c}{V} \exp(-\lambda(1 - y_{BZ})) \tag{18}$$

B_1, B_2 and B_3 are lumped constants given in Eqs. (8)–(10) above. Similar assumptions made for the proposed model equations in catalyst activity decay function based on time on stream (TOS) are also applicable in this model.

Eqs. (16)–(18) contain five parameters, k_1, k_2, E_1, E_2, and λ which are to be determined by fitting into experimental data.

4.2. Determination of model parameters

The kinetic parameters k_{0i}, E_i, and α for the ethylation reaction for both benzene to ethanol molar ratios of 1:1 and 2:1 were obtained by fitting experimental results into the rate Eqs. (5)–(7) using non-linear regression (MATLAB package). The values of the model parameters along with their corresponding 95% confidence limits (CLs) are shown in Tables 5 and 6 (TOS model), while the resulting cross-correlation matrices are also given in Tables 7 and 8. From the results of the kinetic parameters presented in Table 5, it is observed that catalyst deactivation for the feed mole ratio of 1:1 (benzene/ethanol) was found to be small, $\alpha = 0.025$, indicating low coke formation in agreement with the data shown in Table 4, indicating very low coke yield. It can also be observed from Tables 5 and 6 that E_1 for the feed mole ratio of 1:1 (ben-

Table 8
Correlation matrix for ethylbenzene ethylation (TOS model) (feed ratio = 1:1 (benzene:ethanol)).

	k_2	E_2	α
k_2	1.0000	−0.3331	0.7932
E_2	−0.3331	1.0000	−0.0517
α	0.7932	−0.0517	1.0000

Table 9
Estimated kinetic parameters based on reactant conversion (RC-model). Feed ratio = 1:1 (benzene:ethanol).

Parameters	Values		
	k_1	k_2	λ
E_i (kJ/mol)	32.28	8.59	2.083
95% CL	0.92	1.91	0.739
$k_{0i}{}^a \times 10^3$ [m^3/(kg of catalyst s)]	0.0085	0.0553	
95% CL $\times 10^3$	0.0025	0.0167	

^{a} Pre-exponential factor as obtained from Eq. (8); unit for second-order (m^6/kg of catalyst s).

Table 10
Correlation matrix for benzene ethylation (reactant conversion (RC) model) (Feed ratio = 1:1 (benzene:ethanol)).

	k_1	E_1	λ
k_1	1.0000	0.6526	0.9900
E_1	0.6526	1.0000	−0.6601
λ	0.9900	−0.6601	1.0000

Table 11
Correlation matrix for ethylbenzene ethylation (reactant conversion (RC) model) (Feed ratio = 1:1 (benzene:ethanol)).

	k_2	E_2	λ
k_2	1.0000	0.3191	0.9846
E_2	0.3191	1.0000	−0.3552
λ	0.9846	−0.3552	1.0000

Fig. 13. Ethylbenzene yield vs. benzene conversion at various temperatures.

zene/ethanol) is higher than the E_1 for the feed mole ratio of 2:1 (benzene/ethanol), which indicates that the activation energy required to attach activated ethyl cations to an activated benzene molecules as a result of benzene ethylation for the feed mole ratio of 1:1 is higher than that for 2:1 (benzene/ethanol) by 4–5 kJ/mol. Furthermore, it was also noted that the activation energy for the ethylation of ethylbenzene (E_2) for the feed mole ratio of 2:1 is higher than the E_2 for the feed mole ratio of 1:1 (benzene/ethanol). This can be easily understood as the increased dilution of ethanol by benzene reduces the accessibility of EB to yield subsequent alkylated products.

Next, a non-linear regression involving Eqs. (16)–(18), the same experimental data as used with the TOS model, and three adjustable parameters was considered using MATLAB software. Table 9 reports the parameters obtained while the resulting cross-correlation matrices are also given in Tables 10 and 11. Based on the parameters obtained with the RC model in Table 9, it goes to show the accuracy and soundness of the kinetic parameters obtained using the TOS model. Table 7 shows the very low correlations between k_1 and E_1 and E_1 and α and the moderate correlation between k_1 and α. Similar to Tables 7 and 8, reports the very low correlations between k_2 and E_2 and E_2 and α and the moderate correlation between k_2 and α. Table 10 shows the low correlation between k_1 and E_1 and a moderate correlation between E_1 and λ, while Table 11, reports the low correlations between k_2 and E_2 and E_2 and λ and the moderate correlation between k_2 and λ. It can be observed that in the cross-correlation matrices presented in this study, most of the coefficients remain in the low level with only a few exceptions.

Table 12 shows the comparison between the previously reported energies of activation for benzene ethylation and that of the present study. From the results of the activation energies presented in Table 12, it is observed that, value of our activation energy for benzene ethylation is lower than the one reported by Barman et al. [1] who obtained an apparent energy of activation of 56 kJ/mol for alkylation of benzene over cerium exchanged NaX zeolite catalyst. Barman et al. [1] investigations were carried out in a fixed-bed reactor at much lower temperatures of 225–275 °C. Similarly, Sridevi et al. [5] reported an apparent activation energy of 60.03 kJ/mol for alkylation of benzene with ethanol over AlCl$_3$-impregnated 13X zeolites catalyst in a fixed-bed reactor but at much higher temperatures of 400–450 °C.

It is important to point out the significant difference between the activation energies for benzene ethylation (34.69 and 29.95 kJ/mol) and ethylbenzene ethylation to form diethylbenzene (9.53 and 11.03 kJ/mol) for both molar ratios. However, this is not unexpected because it is consistent with the observation made by Kaeding [45] that alkylation, dealkylation and disproportionation reactions of long substituted benzenes generally occur with greater ease compared to their shorter substituted counterparts. This is also in agreement with the observation made by Al-Khattaf et al. [46] in their study of catalytic transformation of three methylbenzenes (toluene, m-xylene and 1,2,4-trimethylbenzene) over USY-based FCC zeolite catalyst in a riser simulator. They noticed that the sequence of reactivity of the alkylbenzenes decreases as the number of methyl group per benzene ring decreases.

To check the validity of the estimated kinetics parameters for use at conditions beyond those of the present study, the fitted parameters were substituted into the comprehensive model developed for this scheme and the equations were solved numerically using the fourth-order-Runge-Kutta routine. Graphical comparisons between experimental and model predictions for the time

Table 12
Activation energies at different reaction conditions.

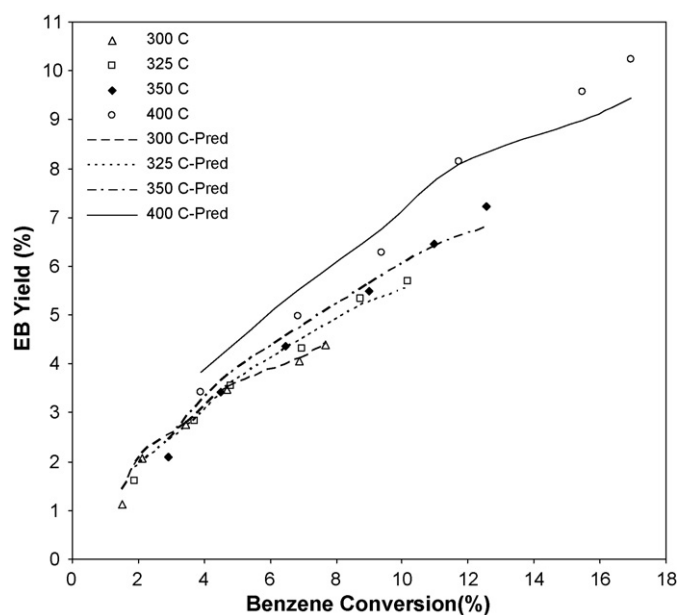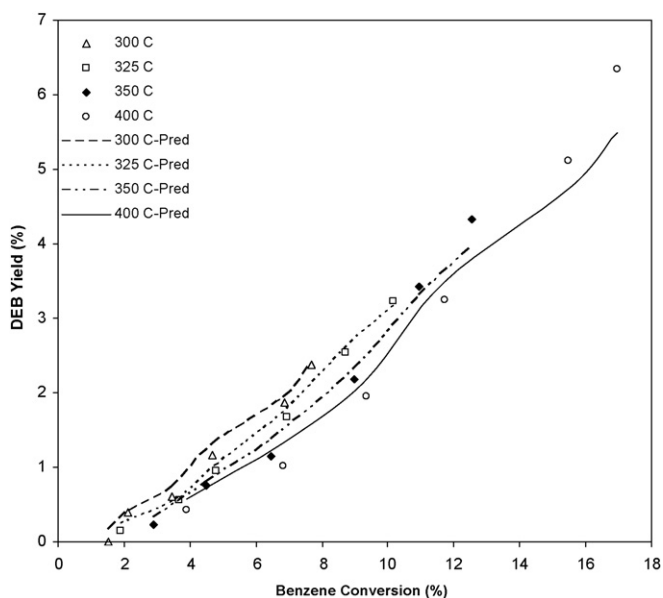| References	Activation energy (kJ/mol)	Catalyst	Reactor	Benzene to ethanol molar ratio	Temperature range (°C)
Sridevi et al. [5]	60.03	AlCl$_3$-impregnated 13X zeolite	Fixed-bed	3:1	400–450
Barman et al. [1]	56.00	Cerium exchanged NaX zeolite	Fixed-bed	3:1	225–275
Present study	34.69	ZSM-5 zeolite	Fluidized-bed	1:1	300–400

Fig. 14. Diethylbenzene yield vs. benzene conversion at various temperatures.

on stream model (TOS) based on the optimized parameters for Scheme 1 are shown in Fig. 4. It can be seen that the model predictions compared very well with the experimental data. Further comparisons between model predictions and experimental data also based on time on stream model are presented in Figs. 13 and 14. As observed in these plots, the model predictions compares favourably with the obtained experimental data for the various conditions, indicating the model can be used to accurately represent the experimental data following the assumptions made, coupled with the peculiar nature of this process in the riser simulator. In addition, the reconciliation plot (Fig. 15) between the experimental data and the model predictions for the time on stream model, display a normal distribution of residuals, besides, the adequacy of the model and the selected parameters to fit the data as shown in Tables 5 and 6 gave 0.9921 regression coefficients.
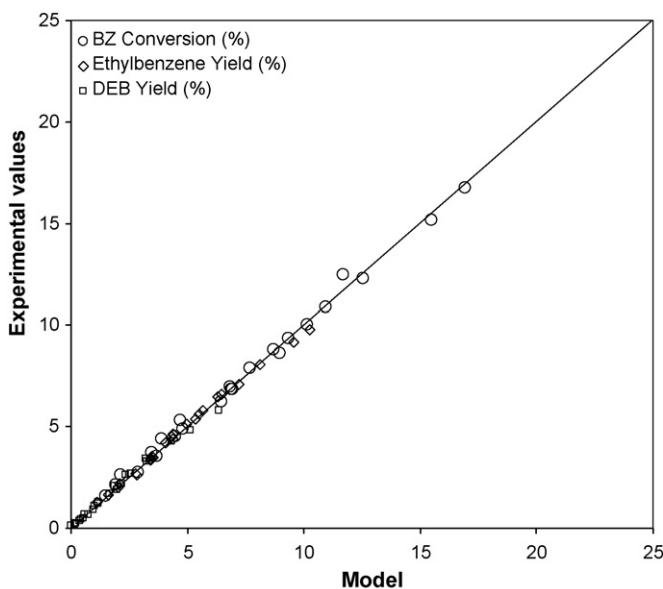

Fig. 15. Overall comparison between the experimental results and model predictions.

5. Conclusions

The following conclusions can be drawn from the ethylation reaction of benzene with ethanol over ZSM-5 based catalyst. The study was carried out over the temperature range of 300–400 °C. The experimental results were modeled over the fresh catalyst based on a comprehensive reaction scheme using the time on stream model. The following summarizes our major findings:

(1) Significant benzene conversion, ethylbenzene yield and diethylbenzene yield were achieved, despite the short reaction times used (3–15 s). Both benzene conversion, ethylbenzene yield and diethylbenzene yield were found to increase with reaction temperature and time.
(2) The maximum benzene conversion of 16.95%, gave an ethylbenzene selectivity and diethylbenzene selectivity of 60.41 and 37.40%, respectively, at 400 °C at a reaction time of 15 s for 1:1 (benzene/ethanol) molar ratio.
(3) Alkylation of benzene is the primary reaction that resulted in the formation of EB. While, the secondary ethylation reaction produced the diethylbenzene.
(4) The conversion of benzene shows a significant decline with increasing feed mole ratio of benzene to ethanol from 1:1 to 3:1. The selectivity for EB improved with an increase in the ratio of benzene to ethanol.
(5) The ratio of ethylbenzene/DEB in the reaction product was found to decrease as temperature was increased from 300 to 400 °C. This indicates that the alkylation of ethylbenzene with ethanol to form diethylbenzene is highly sensitive to temperature. Also, this ratio was found to increase with increasing feed ratios of benzene to ethanol.
(6) Partial deactivation of the active sites on the external of the catalyst crystal due to precoking was found to have a significant effect on the P/O ratio.
(7) Kinetic parameters of the benzene ethylation (E_1) and ethylbenzene ethylation (E_2) with ethanol were calculated using the catalyst activity decay function based on time on stream (TOS). The apparent activation energies were found to decrease as follows: $E_1 > E_2$.
(8) Increasing feed mole ratio of benzene to ethanol, was found to decrease E_1 (benzene ethylation) and increase E_2 (ethylbenzene ethylation).

Notation

C_i	concentration of specie i in the riser simulator (mol/m^3)
CL	confidence limit
E_i	apparent activation energy of ith reaction (kJ/mol)
k_1	rate constant of reaction 1 (m^3/kg$_{cat}$ s)
k_2	rate constant of reaction 2 (m^3/kg$_{cat}$ s)
k	apparent kinetic rate constant (m^3/kg$_{cat}$ s)
k_0	pre-exponential factor in Arrhenius equation defined at an average temperature [m^3/(kg$_{cat}$ s)], units based on first-order reaction
MW_i	molecular weight of specie i
R	universal gas constant (kJ/(kmol K)
t	reaction time (s)
T	reaction temperature (K)
T_0	average temperature of the experiment (343.75 °C)
V	volume of the riser (45 cm^3)
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 ith component (wt%)

Greek letters

α apparent deactivation constant (s^{-1}) (TOS model)

η effectiveness factor (dimensionless)

Subscripts

0   at time $t = 0$

1   for reaction (1)

2   for reaction (2)

cat   catalyst

i for ith component

Acknowledgements

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