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Effect of N$_2$ and O$_2$ on selective disproportionation of xylene mixed ethylbenzene over highly active silylated HZSM-5

Kakasaheb Y. Nandiwale · Vijay V. Bokade

Abstract The influence of carrier gases such as nitrogen and air (78 % N$_2$ and 21 % O$_2$) on catalytic activity and its stability etc., over modified H-ZSM-5 (pore size regulated by silylation) for the selective formation of *Para*-diethylbenzene (*p*-DEB) by xylene mixed ethylbenzene (EB) disproportionation is discussed. The comparison of plane and modified HZSM-5 catalysts using different carrier gases viz., nitrogen and air on pure EB and xylene mixed EB feeds are presented. The disproportionation reaction with xylene mixed EB feed in the presence of air over HZSM-5TS (8 % silica deposited) is observed to be more active and selective as far as *p*-DEB formation is concerned. Reaction kinetics of EB disproportionation with first-order power law model at different temperatures and *W/F* (weight of the catalyst/reactant feed rate), with pure EB and xylene mixed EB feed are also discussed. The reaction rate constants are within 0.0668–0.0969 dm^3/g h and the activation energy of the reaction is calculated to be 30.16 kJ/mol. The catalyst stability (100 h) in the presence of carrier gas is also studied in detail.

Keywords H-ZSM-5 · Silylation · Ethylbenzene · Disproportionation · Carrier gas · Kinetics

Introduction

The shape-selective disproportionation of ethylbenzene over pore size controlled zeolite catalysts to produce isomers of diethylbenzene, among other products, has got

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great attention recently [1]. This is due to the plentiful applications of these compounds in a variety of industrial processes [2]. *Para*-diethylbenzene (*p*-DEB), which is the most important among the three diethylbenzene isomers, is an important desorbent in adsorptive separation processes such as UOP Parex, IFP eluxyl [1–3]. Moreover, it is an important monomer for the production of copolymers, such as ion exchange resins and viscosity modifiers of lubricant oil [4]. Zeolites are solid acid catalysts and considered as one kind of efficient, safe and environmentally benign catalysts which can replace liquid acids in chemical industries [1].

In most of the cases, the composition of the different diethylbenzene isomers in the reaction product was limited by thermodynamics, which led to less amount of the *para*-isomer, compared to the *meta*-isomer (*meta*-diethylbenzene, abbreviated as *m*-DEB). It has been reported that the mechanism of zeolite-catalyzed ethylbenzene disproportionation is shape selective with the diffusion difference among *p*-DEB, *m*-DEB, and *ortho*-diethylbenzene (*o*-DEB) [5]. Hence, catalyst modification techniques such as partial deactivation of external surface acid sites, narrowing of pore channels, increasing diffusion path length (crystal size), etc., have been used to enhance *p*-DEB selectivity during ethylbenzene disproportionation. The diffusion affects the selectivity of the individual isomers of diethylbenzene formed by ethylbenzene disproportionation. This is due to different diffusion lengths of diethylbenzene isomers. To improve *p*-DEB selectivity, the acidity and structure of zeolite is necessary to be modified. On one hand, modification passivates the acidic sites on the external surface of ZSM-5 for eliminating secondary isomerization of *p*-DEB. On the other hand, modification reduces opening sizes of ZSM-5 for distinguishing diffusivities among *p*-DEB, *m*-DEB and *o*-DEB. So, it is highly

desirable that the high selectivity can be achieved with a maximum reactivity by the proper modification. SiO_2-CVD (chemical vapor deposition) with tetraethyl-orthosilicate (TEOS) is an important method for improving shape-selectivity of zeolite. SiO_2-CVD/ZSM-5 showed improved p-DEB selectivity [6, 7]. In preparation of the commercial catalyst for the shape-selective disproportionation of toluene to para-xylene, the pre-coking method has been replaced by SiO_2-CLD (chemical liquid deposition). Compared with CVD, CLD may be more easily transferred to an industrial preparation in large scale, such as SiO_2-CLD modification of ZSM-5 with poly-siloxane in MTPX process [8].

A practical way of easing the transport of the reactants and products through the zeolite catalyst and prolonging catalyst activity was to incorporate appropriate carrier gases (or diluent gases) during the reaction. The carrier gas serves as a diluting medium to improve the conductivity and diffusivity of the reactant and product molecules through zeolite intracrystalline pores or voids. The reactants, reaction intermediates and products, if retained in the interior of zeolite channels or pores, can affect the size/shape selectivity of the catalyst and hence are equally credible to increase coke formation [9–14]. Hence, the reaction chemistry of hydrocarbons in zeolite catalysts cannot be understood by monitoring the products alone.

The influences of carrier gases on catalytic activity and stability of zeolites in monoalkylbenzene disproportionation reaction have been the focus of several studies [9, 15–18] in which hydrogen (H_2) and nitrogen (N_2) were the two most popular candidates for the study of CGE (carrier gas effect). For example, the effect of H_2 carrier gas on catalytic activity has been reported by Gnep and Guisnet [15] for toluene conversion on mordenite zeolite and for ethylbenzene disproportionation on 0.2 wt% Pt/LaNaX zeolite. The decrease in catalytic activity is attributed either due to the decrease in the concentration of intermediate benzylic carbocations [15, 16] or the decrease in Brønsted acidity; both interpretations need the activation of molecular H_2. Schulz-Ekloff et al. [17] investigated the variations of the catalyst conversion rate in the existence of different carrier gases. The authors disclosed that, under elevated pressures (>0.1 MPa), the degree of conversion during toluene disproportionation on H-ZSM-5 follows the trend $H_2 < He < N_2 < Ar$. Chen et al. [9] reported the influence of carrier gases (N_2, H_2, He, CO_2) on the catalytic activity, stability, and coke formation in zeolite beta during cumene disproportionation reaction. The authors disclosed that the degree of conversion during cumene disproportionation on zeolite beta follows the trend $N_2 > H_2 > He > CO_2$, whereas order was reverse for catalytic stability.

Our earlier published literature [19] on EB disproportionation demonstrated the advantages of silica-deposited HZSM-5 over plane HZSM-5. The reported study also explains in detail about the degree of silylation, use of pure EB and xylene mixed EB feed and its comparison along with simple reaction kinetics.

But the reported literature [19] is having lack of information on use of carrier gas such as pure N_2 and air (78 % N_2, 21 % O_2, and 1 % others) and its effect on the activity, selectivity and stability of silylated HZSM-5. This study is crucial to get stable activity data to make the process economical. The presence of xylene isomers in the feed is expected to hamper the catalytic activity by deposition of these isomers/byproducts or coke formation, which affects the stability of catalyst. We have not come across any literature on the study of effect of carrier gases on the catalytic activity and stability, using xylene mixed EB feed. This presented study highlights all these issues. The present paper also involves the reaction kinetics and interpretation of experimental data on effect of carrier gas and other process parameters, including stability study of catalyst (100 h) using N_2 and air as carrier gas. In this study, we have used 8 % silylated HZSM-5 (HZSM-5TS) as catalyst, which is an optimum catalyst obtained from our earlier study [19].

Experimental section

Catalyst synthesis and modification

NaZSM-5 catalyst with SiO_2/Al_2O_3 ratio of 250 was synthesized as per the reported procedure [19] and analyzed by XRF. The hydrogen form of the sample (HZSM-5) was obtained by ammonium exchange with 1 M ammonium nitrate solution followed by drying and calcination at 823 K. The silylation of HZSM-5 was performed according to reported procedure [19]. For silylation, the calcined HZSM-5 sample was refluxed in a mixture of 20 % tetraethyl ortho silicate (TEOS) +35 % methanol +45 % toluene at 353 K for 12 h. The presence of methanol generates dimethyl ether and water on acid sites, which helps in the hydrolysis of TEOS at 353 K. After 12 h, the sample was washed to remove any loosely adsorbed TEOS on the surface and dried in an oven for 2 h at 393 K and calcined at 823 K to obtain 4 % silica deposited on the catalyst sample. The same procedure was repeated twice to obtain catalyst samples with 8 % (HZSM-5TS).

The weight of silica deposited was obtained by the formula:

$$[(\text{Weight of the sample after silylation} \\ - \text{weight of the sample before silylation})/ \\ \text{weight of the sample before silylation}] \times 100 \quad (1)$$

Reaction procedure

All reactions were carried out in a fixed bed catalytic reactor, made of SS 316 (1.8 cm I.D. × 30 cm height), at atmospheric pressure containing 10 g of fresh catalyst sample. The catalyst section was packed in the middle between two sections of glass wool. Porcelain beads were loaded at the top of the catalyst bed to preheat the feed. Before start of reaction, the catalyst was activated at 773 K for 10 h in the flow of air. After completion of activation, flow rate of carrier gas was controlled through a mass flow controller at 40 mL/min, an optimum rate from previous studies [19]. The mass flow controller was calibrated carefully with a soap film as well as with a wet gas meter for every run.

In the control experiments, the reactant of different compositional xylene mixed EB and pure EB feed for disproportionation was fed from the top of the bed through a calibrated syringe pump (ISCO, Lincoln, NE, USA) into the reactor at the desired reaction temperature in the presence of carrier gas such as air and nitrogen (40 mL/min). The products along with unreacted ethylbenzene were passed through the cold-water condenser attached to the reactor and a gas–liquid separator. In all experiments, the liquid mass balance was observed to be almost 100 %. Each reaction was performed for a time on stream of 5 h and stable fourth hour data are used for the comparison.

Feed and product analysis

The liquid products of EB disproportionation were analyzed in a HP6890 Series GC, using Flame Ionization Detector (FID), in the presence of nitrogen as a carrier gas. The DBWAX capillary column was used for the analysis. The gaseous products were analyzed by Chemito Gas Analyzer 1000 Series, using Thermal Conductivity Detector (TCD). The Spherocarb column of 8' length × 1/8" diameter was used for the analysis.

EB conversion and p-DEB selectivity were calculated from following formulae:

EB conversion (%)

$$= [(\text{EB in feed} - \text{EB in product})/(\text{EB in feed})] \times 100$$

p-DEB selectivity (%)

$$= [(p\text{-DEB in product}/\text{SDEB isomers in product})] \times 100 \tag{2}$$

Results and discussion

Effect of carrier gas on EB disproportionation over pore size regulated HZSM-5

The experiments were carried out in the presence of carrier gases such as nitrogen and air (78 % N_2 and 21 % O_2),

Table 1 Performance comparison for use of different carrier gases using pure EB feed

Catalyst	HZSM-5TS	
Carrier gas	Nitrogen	Air
Product composition (%)		
Benzene	2.69	3.93
Toluene	0.06	0.79
EB	93.27	91.38
ΣXylenes	–	–
ΣC$_9$ Aromatics	–	0.40
m-DEB	0.24	0.13
p-DEB	3.70	3.19
HBF	0.04	0.18
Performance (%)		
EB conversion	6.21	8.62
m-DEB selectivity	6.09	4.00
p-DEB selectivity	93.91	96.08

Reaction conditions: Catalyst weight, 10 g; Catalyst volume, 13 cc; Temperature, 603 K; WHSV, 3 h^{-1}; Feed, Pure EB (99.37 %) HBF, high boiling fractions

using pure ethylbenzene feed. The results of EB Disproportionation over HZSM-5TS (8 % silica deposited) using air (78 % N_2 and 21 % O_2) and nitrogen as carrier gas are tabulated as Table 1. All experiments were performed in duplication and have ±2 % error.

EB conversions were observed to be decreased, in the presence of nitrogen as compared to air (78 % N_2 and 21 % O_2) as carrier gas (Table 1). This decrease in EB conversion with nitrogen may be due to less removal of moisture and/or hydrocarbons, which are present on the catalyst surface and also by deposition of nitrogen molecules on the catalyst active surface. The removal of these foreign materials/hydrocarbons by air makes the catalyst surface more activated and was reflected by increase in EB conversion. No oxygenated compounds were detected in the presence of air.

In nitrogen as carrier gas, the isomerization of m-DEB to p-DEB is less as compared to air as carrier gas. This less isomerization reaction with nitrogen may be due to the suppression of active surface by the adsorption of nitrogen molecules, which reduces the isomerization of m-DEB to p-DEB.

The study was further extended to see the effect of carrier gases using pure and xylene mixed ethylbenzene (EB) feed over HZSM-5TS catalyst.

Effect of carrier gases on disproportionation of EB with different compositional feed over HZSM-5TS

The detailed study was carried out on HZSM-5TS using air and nitrogen as carrier gas. The HZSM-5TS in presence of

Table 2 Performance comparison for EB disproportionation using xylene mixed EB feed over HZSM-5TS

Catalyst	HZSM-5TS	
Carrier gas	Air	Nitrogen
Product composition (%)		
Benzene	5.15	1.73
Toluene	0.89	0.78
EB	52.89	56.51
$\sum$Xylenes	35.78	35.86
$\sum C_9$ Aromatics	0.41	0.25
m-DEB	0.07	0.17
p-DEB	4.71	4.64
HBF	0.10	0.06
Performance (%)		
EB conversion	11.11	7.49
m-DEB selectivity	1.61	3.53
p-DEB selectivity	98.53	96.46

Reaction conditions: Catalyst, HZSM-5TS; Catalyst weight, 10 g; Catalyst volume, 13 cc; Temperature, 603 K; Feed, 64 % EB and 36 % Xylene isomers

air and nitrogen was studied for the EB disproportionation using pure EB (Table 1) and xylene mixed EB feed (Table 2).

The increase in EB conversion was observed using xylene mixed EB feed. It is reported that, ethylbenzene conversion and the yield of p-DEB increase with the enhancement in m-xylene concentration [20]. The increase in EB conversion was observed, in the presence of air as represented in Table 2. The increase in EB conversion in the presence of air as carrier gas may be due to the more removal of moisture/any foreign materials deposited on the catalyst surface and makes the catalyst surface more active and also the presence of O_2 in air helps for auto thermal reaction. The formation of less m-DEB with nitrogen carrier gas catalyst may be due to less EB conversion. The increase in p-DEB selectivity was observed, may be due to the enhancement in the isomerization reaction with air as carrier gas. This enhancement in the isomerization reaction may be due to the narrow-down of the pore mouth of the catalyst, by blocking some external acid sites.

Effect of weight hourly space velocity (WHSV)

The use of air and nitrogen as carrier gas was studied in detail. Based on the observation, the air as carrier gas was observed to be more selective for the formation of p-DEB. Table 3 represents the effect of weight hourly space velocity (WHSV), for the air as carrier gas using pure and xylene mixed EB feed. The EB conversion was observed to be decreased (from 23.69 to 3.76 %, for pure EB and from

24.69 to 9.26 % for mixed EB), with increase in WHSV from 1 to 4 h^{-1}, for both the EB feeds. This decrease in EB conversion with increase in WHSV may be due to less contact time. With increase in WHSV, the m-DEB formation was also observed to be decreased from 22.15 to 1.62 % and from 14.76 to 1.67 %, for pure and mixed EB feed, respectively. This decrease in m-DEB formation with increase in WHSV may be due to the less external surface reaction, due to less contact time and increase in isomerization reaction of m-DEB to p-DEB. The p-DEB selectivity was observed to be increased from 77.84 to 98.37 % and from 85.23 to 98.53 %, for pure and mixed EB feed, respectively, with increase in WHSV. The increase in p-DEB selectivity, with increase in WHSV, may be due to the enhancement of isomerization reaction of m-DEB to p-DEB by increase in the rate of diffusion from external to the internal surface of the catalyst.

Stability of HZSM-5TS in presence of carrier gas

The reaction stability was monitored for both the carrier gases (nitrogen and air) for HZSM-5TS catalyst. Each reaction was carried out for more than 100 h on stream, represented by Fig. 1. The mixed EB feed was used for the reaction. Without carrier gas, the EB conversion was found to be decreased to <6 % at p-DEB selectivity in the range of 91–92 %. The EB conversion was observed to be stabilized to ~10 % and p-DEB selectivity to >96 %, for air as carrier gas. The activity (7 %) and selectivity (94 %) was observed to be less for N_2 as carrier gas. This concluded that, the presence of O_2 in air enhances the catalytic activity and stability, by means of auto-thermal reaction and also helps to keep the catalyst surface clean by removing any foreign material, nitrogen compounds etc.,

The removal of coke from deactivated catalysts, with addition of O_2, is generally carried out through an oxidative treatment under air flow. The choice of the operating conditions especially temperature is important for limiting the detrimental effect of the water, produced by coke oxidation, on the zeolite catalyst. Above 573 K, all the oxidative compounds undergo decomposition making zeolite surface active and fully accessible [21].

Reaction kinetics

Kinetic runs were carried out in the region free of inter-particle diffusion effects. This was established by runs carried out with constant W/F (space time expressed as grams of catalyst per hour per mole) but varying liquid feed rates. In the case of zeolite-catalyzed reactions two types of diffusion process are considered: (i) macro-pore between the catalyst pellet particles; and (ii) micro-pore inside the

Table 3 Effect of WHSV on disproportionation of EB with different compositional feed with air as carrier gas over HZSM-5TS

Feed	Pure EB				Xylene mixed EB			
WHSV (h^{-1})	1	2	3	4	1	2	3	4
Product composition (%)								
Benzene	11.33	7.15	3.93	1.16	13.26	5.19	5.15	5.86
Toluene	1.54	0.19	0.79	0.04	1.77	0.85	0.89	0.74
EB	76.31	81.72	91.38	96.24	39.31	53.41	52.89	54.74
ΣXylenes	–	–	–	–	36.01	36.00	35.78	35.78
ΣC_9 Aromatics	1.14	0.29	0.40	0.08	1.40	0.44	0.41	0.41
m-DEB	2.14	0.82	0.13	0.04	1.11	0.22	0.07	0.06
p-DEB	7.52	9.66	3.19	2.42	6.41	3.84	4.71	2.20
HBF	0.02	0.17	0.18	0.02	0.73	0.05	0.10	0.16
Performance (%)								
EB conversion	23.69	18.28	8.62	3.76	24.69	10.59	11.11	9.26
m-DEB selectivity	22.15	7.82	4.00	1.62	14.76	5.42	1.67	2.65
p-DEB selectivity	77.84	92.17	96.08	98.37	85.23	94.58	98.53	97.34

Reaction conditions: Catalyst, HZSM-5TS; Catalyst weight, 10 g; Catalyst volume, 13 cc; Temperature, 603 K; Carrier gas, air
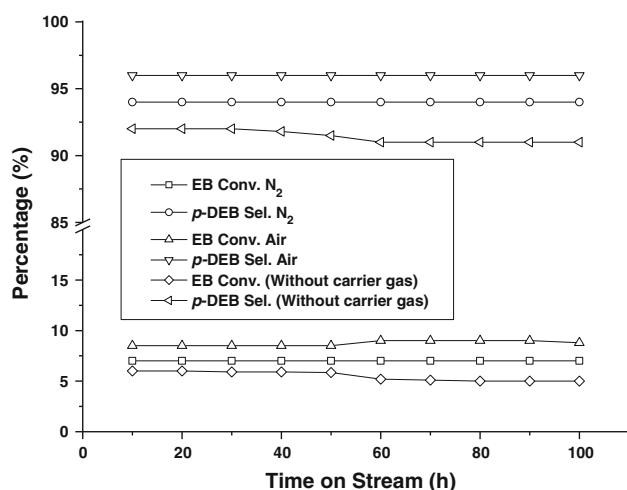

Fig. 1 Stability of HZSM-5TS catalyst. Reaction conditions: Catalyst, HZSM-5TS; Catalyst weight, 10 g; Catalyst volume, 13 cc; WHSV, 3 h^{-1}; Temperature, 603 K

Fig. 2 Conversion of EB over HZSM-5TS with air as carrier gas by xylene mixed EB feed at different W/F and temperatures achieved from first-order kinetic model

zeolite channels. The above experiments for finding the inter-particle diffusion region show only the absence of film diffusion. Since the channel dimensions of modified zeolite are comparable to those of reactant ethylbenzene and product di-ethylbenzenes and benzene, micro-pore diffusion resistance cannot be avoided. Similar kinetic studies were reported for toluene ethylation [20], isomerization of ethylbenzene and m-xylene [22], disproportionation of toluene [23, 24], methylation of toluene [25] and disproportionation ethylbenzene [26–28].

Ethylbenzene disproportionation was carried out at three different temperatures viz: 583, 603 and 623 K, over HZSM-5TS catalyst in the presence of air as carrier gas to collect the kinetic data. At each temperature, W/F was
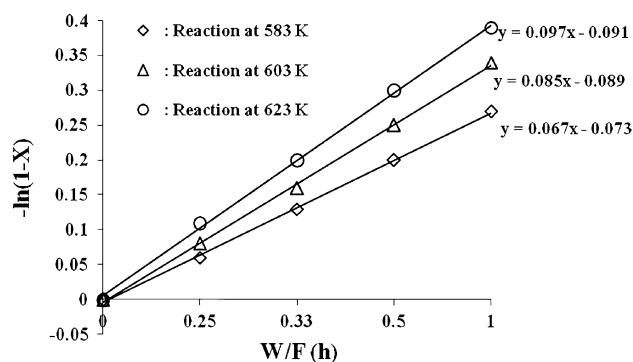
varied to obtain different EB conversions. The first-order dependence of EB concentration with rate, as similar to model proposed by Nayak and Riekert [24] was used:

$$\text{Reaction rate} = -r = dx/d\,(W/F) = k(1-X) \quad (3)$$

where r is the rate of EB conversion, X is EB conversion and W/F is the space time expressed as grams of catalyst per hour per mole. Integration of Eq. (3) gives
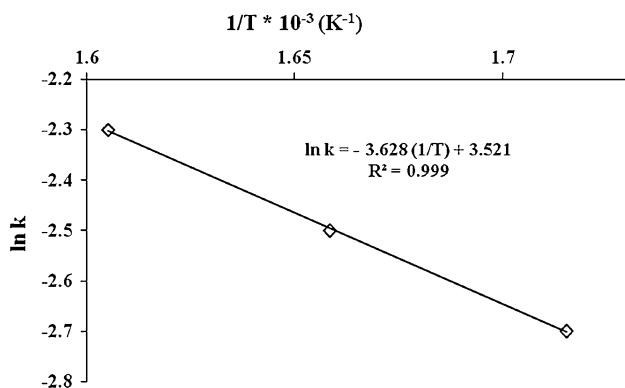
$$-\ln(1-X) = k\,(W/F) \quad (4)$$

The rate constant k can be calculated from a plot of $-\ln(1-X)$ versus W/F.

Figure 2 described the effect of reaction temperature on the rate of reaction. The rate of reaction was observed to be increased with increase in the reaction temperature and W/F. As seen in Fig. 2, the slope and the intercept of the trend lines give the reaction constant and the model integration constant, respectively. Furthermore, it is important to note

Table 4 R^2 value and rate constants for disproportionation of EB at different compositional feed over HZSM-5TS with air as carrier gas

Feed	Reaction temperature (K)	R^2 value of trend line	Rate constant (k) (dm^3 g^{-1} h^{-1})
Xylene mixed EB	583	0.995	0.0668
	603	0.999	0.0849
	623	0.998	0.0969
Pure EB	603	0.999	0.0629

Table 5 Kinetic studies on ethylbenzene disproportionation reaction

Catalyst	Activation energy (kJ Mol^{-1})	References
ZSM-5-based	26.27	[26]
ZSM-5-based	85	[27]
Ultrastable Y (USY)-zeolite-based	35.51	[28]
ZSM-5-based	30.16	Present case

Fig. 3 Arrhenius plot for first-order kinetic model for disproportionation of EB over HZSM-TS with air as carrier gas by xylene mixed EB feed

Fig. 4 First-order kinetics of EB disproportionation with different compositional feed over HZSM-5TS with air as carrier gas at different W/F

that the values of R^2 of the trend lines presented in Table 4 give the confidence levels of the reaction with the first-order kinetic model.
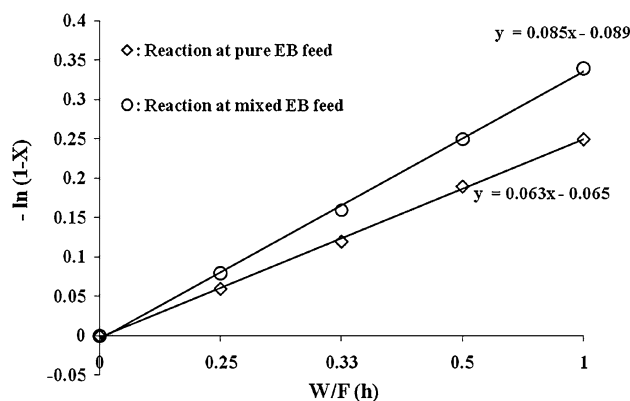
Table 4 represents the rate constants of first-order model, which was calculated from slope of the trend lines in Fig. 2. The rate constant at 583 K was found to be 0.0668 dm^3 g^{-1} h^{-1} and it increased to 0.0969 dm^3 g^{-1} h^{-1} at 623 K which clearly indicates that elevated temperatures accelerate disproportionation and reduce reaction duration to achieve maximum product. The rate constants obtained in this work were obviously within the range reported by other researchers [26–28]. The first-order rate constant obtained does not take into consideration the deactivation of modified HZSM-5 due to coke formation. This is justified, because catalyst stability runs showed a steady activity without any sign of decrease in conversion with a time on-stream period of 100 h. If the temperature dependence of the rate constant is expressed in Arrhenius form,

$$k = k_o \exp(-E/RT) \tag{5}$$

where, k_o is the frequency factor, E the activation energy, R the gas constant, and T the temperature, by plotting ln k versus $1/T$, the activation energy E can be obtained from the slope. Similar types of Arrhenius plots are reported by Shahla et al. [29].

Based on Eqs. (4), (5) and Fig. 3, the calculated activation energy of the disproportionation of ethylbenzene is 30.16 kJ mol^{-1} which also agreed well with reported value (Table 5).

The increase in rate of reaction is observed with xylene mixed EB feed as compared to pure EB feed with increase in W/F as represented by Fig. 4. The rate constant for pure EB feed was found to be 0.0629 dm^3 g^{-1} h^{-1} and that of xylene mixed EB feed was 0.0849 dm^3 g^{-1} h^{-1} at 603 K which clearly indicates that xylene mixed EB feed accelerates disproportionation reaction.

Conclusions

The effect of carrier gases such as air (78 % N$_2$ and 21 % O$_2$) and nitrogen on the selective formation of p-DEB by EB disproportionation reaction was studied in detail. The performance of the air (78 % N$_2$ and 21 % O$_2$) and nitrogen on catalyst was compared for the HZSM-5 (plane) and modified HZSM-5 catalyst for the EB disproportionation reaction. The different types of feed viz: pure EB (99 %) and xylene mixed EB (64 % EB and 36 % xylene isomers), were used for the comparative study of carrier gases. The stability study reveals that, the presence of air over HZSM-

5TS (8 % silica deposited) was observed to be more active and selective as far as EB conversion (10 %) and *p*-DEB (96 %) formation is concerned. The presence of O_2 in carrier gas accelerates the auto-thermal reaction which in turn increases EB conversion and delays coke formation.

The disproportionation reaction follows the first-order kinetics with respect to *W/F* (weight of the catalyst, g/feed rate, g/h). The rate constants and activation energy (30.16 kJ mol^{-1}) obtained are within the range of reported value.

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