



Journal of Applied Sciences

ISSN 1812-5654

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The Role of Acid Strength of Modified NaX Zeolites on Gas Phase Ethylation of Benzene

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Abstract: The role of acid strength of modified NaX zeolites in gas phase ethylation of benzene were studied over Ce exchanged NaX zeolite of different types. Acidity of the modified zeolite was investigated by means of adsorbing ammonia at different temperature. The conversion of reactants varies with the acid strength as well as the different types of the zeolites. The strong acid sites are active centers while the weak acid sites are inactive. The influences of various process parameters such as temperature, space-time and the feed ratio of benzene to ethanol on benzene conversion over most acidic zeolite were studied. The kinetic and adsorption constants of the rate equations were estimated by the best fit. From the estimated kinetic constants, the activation energies and frequency factors for various reactions were determined. The activation energy values compared well with those reported by other investigators for same reactions over similar catalysts.

Key words: Alkylation, acidity, ethyl benzene, Ce-exchanged, kinetics

INTRODUCTION

The role of acid strength of zeolites in gas phase ethylation of benzene were studied over Ce exchanged NaX zeolite of different types by means of adsorbing ammonia at different temperature. The strong acid sites are active centers while the weak acid sites are inactive. Ethyl benzene is commercially important as an intermediate for the manufacture of styrene. Styrene is an important monomer in the production of synthetic rubber, synthetic plastics and resins. Ethyl benzene has also a limited use as a solvent and for the production of dyes. The process of alkylation of benzene with ethylene on Friedel-Craft's catalysts is a traditional one and accounts for more than 90% of ethyl benzene production. The use of these catalysts, however, gives rise to many problems such as handling, safety, waste disposal and corrosion. Recently, much effort has been put on developing alternative environment-friendly catalyst systems. Zeolite based catalysts are gaining importance in this respect and have been replacing the conventional catalysts. The vapor phase alkylation of benzene with ethylene in the presence of ZSM-5 zeolite is the famous Mobil-Badger process, which is now in commercial practice for the production of ethyl benzene. The direct use of ethanol, instead of ethylene, as an alkylating agent with benzene for this reaction has some advantages. It is known that ethylene is a major source of carbonaceous deposits in alkylation reactions in the vapor phase over the solid catalyst. A long stable life of the catalyst is observed

when ethyl alcohol rather than ethylene is used as the alkylating agent. In addition to the academic interest, the direct use of ethanol in the manufacture of ethyl benzene is also of economical significance to those countries where biomass derived alcohol is an additional raw material for the manufacture of chemicals. In the present study, a detailed study has been performed on the synthesis of ethyl benzene over cerium exchanged NaX zeolite in a fixed-bed reactor.

Studies on alkylation reactions over ZSM type zeolites have been reported by several (Anderson *et al.*, 1979; Bhat *et al.*, 1998; Chandavar *et al.*, 1982; Fraenkel and Levy, 1989; Lee and Wong, 1985) researchers. However, only a few researchers have performed alkylation reactions of aromatics on the alkali metal forms of X type zeolite (Engelhardt *et al.*, 1987; Garces *et al.*, 1985). Alkylation of benzene with ethanol has also been studied over AlCl₃-impregnated 13X zeolite (Sridevi *et al.*, 2001). Replacement of Na ions of synthetic zeolites with polyvalent cations from rare earth metals (La, Ce, etc.) has been reported to give materials of superior catalytic activity (Rabo *et al.*, 1961; Hunter and Scherzer, 1971). Alkylation of benzene with isopropanol has also been carried out over rare earth modified H-beta zeolite (Jia *et al.*, 1992) and rare earth exchanged faujasite Y (Naum *et al.*, 1987). However, there is no report in the literature on benzene ethylation over rare earth exchanged X-type zeolite, which is most common. It was, therefore, thought desirable to study the benzene ethylation reaction over Ce-exchanged NaX zeolite. A further

objective of the present study was to develop a kinetic model so as to obtain an intrinsic rate equation for this commercially important reaction.

MATERIALS AND METHODS

Materials: The NaX zeolite used in the present study was obtained from SD. Fine Chemicals Pvt. Ltd., India. It was in the form of 1.5 mm extrudate. Ethyl alcohol and benzene used in this study were of Analytical Reagent grade. Ethyl alcohol was obtained from Qualigens Fine Chemicals, Mumbai, India and benzene from M/s. E. Merck (India) Ltd., Mumbai, India.

Catalyst preparation: The NaX zeolite was first calcined to remove moisture and kept ready for cation exchange. The catalyst particles were first heated with 2% NH_4NO_3 solution at 363 ± 10 K for 6 h, for three times, each time with a fresh 2% NH_4NO_3 solution with subsequent calcining of the particles at 623 K in between. The catalyst particles thus obtained after a total of 18 h heating and containing about 5-6% of Na (determined by flame photometer) were boiled with a required percentage of cerium ammonium nitrate solution for about 16 h, thereby modifying the HX zeolite (Plank *et al.*, 1964; Krishnan *et al.*, 2002). This was then dried and calcined at 623 K and ready for use in the reactor. The X-ray diffraction pattern of the Ce-exchanged NaX zeolite exactly matched with that of the virgin NaX zeolite, indicating no structural change during ion exchange. Catalysts treated with 2, 5, 7, 10 and 12% cerium nitrate solutions were designated as CeX_2 , CeX_5 , CeX_7 , CeX_{10} and CeX_{12} , respectively.

Temperature Programmed Desorption (TPD) of ammonia: Ammonia TPD of the modified catalysts was performed in a CHEM-BET 3000 instrument (Quanta Chrome, USA). In a typical experiment, 0.1 g of the catalyst sample was first degassed at 723 K for 1 h with nitrogen flow. The sample was then cooled to 303 K and at this temperature the gas flow was changed to 1 mol% ammonia in nitrogen for 1 h. The catalyst sample was then heated to 373 K and kept at that temperature until the steady state was attained. The sample was then heated from 373 to 1173 K at a heating rate of 10 K min^{-1} . The desorbed ammonia was detected by a TCD analyzer.

Experimental procedure and product analysis: The catalytic experiments were carried out in a fixed-bed, continuous down-flow, cylindrical stainless steel (SS 316) reactor (0.025 m ID and 0.33 m in length). The reactor was fitted with a preheater in the upstream and a condenser at

its outlet. The reactor was heated electrically from outside and insulated to prevent heat loss. In a typical run, about 0.03 kg of catalyst was loaded into the reactor and supported by inert beads on either side of the bed. The bed temperature was measured by a thermocouple placed in a thermo well extending from the top of the reactor to the centre of the bed. The catalyst was activated *in situ* for 8 h in an atmosphere of nitrogen before the experimental runs were started. The aromatic-alcohol mixture was introduced with the help of a metering pump and vaporized in the preheater before contacting the catalyst. The reactant vapors along with carrier gas (nitrogen) entered the reactor from the top. The desired pressure was adjusted with the help of a needle valve at the bottom of the reactor and read from a pressure gauge fitted at the top of the reactor. The product vapors, along with unreacted reactants, were condensed in a condenser and the liquid samples collected were analyzed in a Gas Chromatograph unit fitted with a 4.2×3.2 mm SS column containing Benton 34 and 7% dinonyl phthalate stationary phase on Celite-545 solid support using a flame ionisation detector (FID). The material balance was checked and it was >98%. From the product analysis, ethyl benzene was found to be the only product with no other detectable amount of side products. On the basis of this observation, the conversion of benzene is defined as follows: $X_B = \text{moles of benzene converted} / \text{moles of benzene fed} = Y_{EB} / (Y_B + Y_{EB})$. Where, Y_B and Y_{EB} are the mole fractions of benzene and ethyl benzene, respectively, in the product stream.

RESULTS AND DISCUSSION

Effect of acidity of zeolite on benzene conversion: NaX zeolite was treated to exchange its sodium ions with cerium ions in order to increase its acidity. This exchange was carried out with cerium nitrate solutions of different concentrations. Figure 1 shows a plot of acidity of the Ce exchanged catalysts versus benzene conversion at a benzene-to-ethanol mole ratio of 3:1 and at a temperature of 513 K. From the Fig. 1, the benzene conversion increases with increase in acidity in the NaX zeolite and this is due to stronger acid sites generated by the exchange. Temperature-Programmed Desorption (TPD) of ammonia was studied with NaX as well as Ce-exchanged NaX zeolites and Fig. 2 shows the TPD profiles of the catalysts. The desorption of ammonia corresponding to different peaks is indicative of energy levels at which ammonia is bound to the 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 towards the higher temperatures with

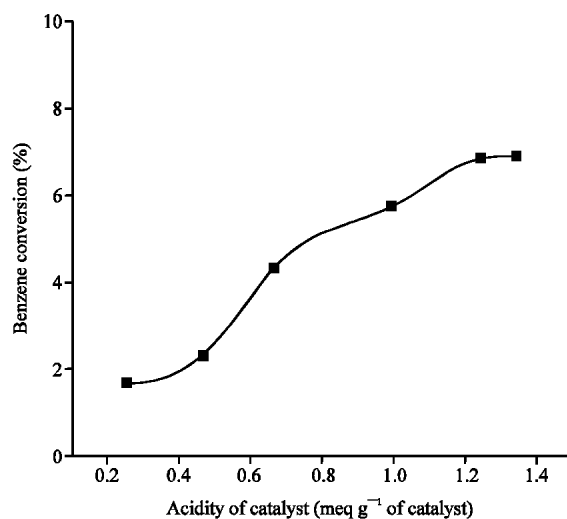


Fig. 1: Effect of acidity of catalyst on conversion of benzene Benzene/EtOH, 3:1; temperature, 513 K; W/F, 19.47 kg h kg mol⁻¹; pressure, 1 atm

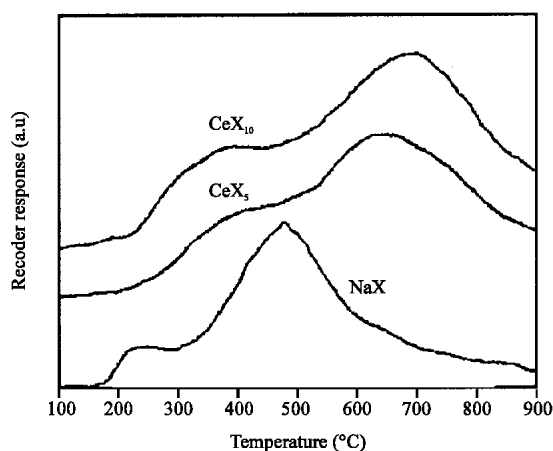


Fig. 2: Temperature programmed desorption profiles of ammonia for NaX, CeX₅ and CeX₁₀ catalysts

replacement of sodium by cerium. Moreover, the number of acid sites also increases as the peak area increases with Ce-exchange. The increase in catalytic activity is, therefore, due to the increase in both quantity and strength of the acid sites by cerium exchange.

Determination of acidity of modified NaX zeolites: Brønsted acidity and Lewis acidity of various catalysts were estimated by the procedures followed by Mendham *et al.* (2000) and shown in Table 1.

Time-on-stream behavior of the catalysts: The stability of various Ce-exchanged NaX zeolites were tested for about

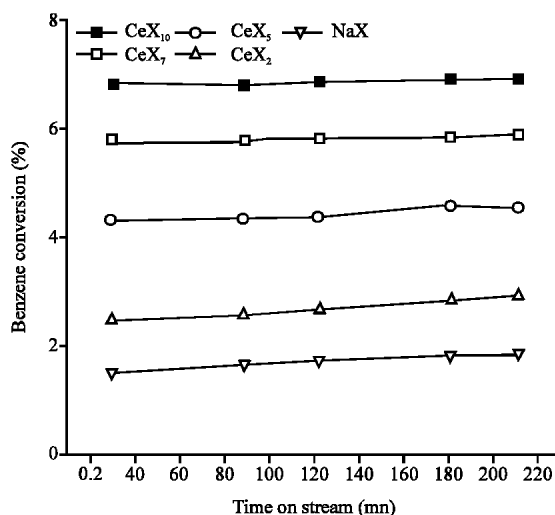


Fig. 3: Time on stream behavior of various catalysts

Table 1: Brønsted and Lewis acidity of various catalyst
Acidity (meq g⁻¹ of catalyst)

Catalyst	Brønsted	Lewis	Total
NaX	0.15	0.10	0.25
CeX ₂	0.26	0.21	0.47
CeX ₅	0.34	0.28	0.62
CeX ₇	0.55	0.45	1.00
CeX ₁₀	0.70	0.57	1.27
CeX ₁₂	0.74	0.62	1.36

3 h time on stream at 513 K and atmospheric pressure. The benzene conversion remained constant during this period as shown in Fig. 3. CeX₁₀ Catalyst gives highest conversion compared to CeX₇, CeX₅, CeX₂ and NaX zeolites. So kinetic study has been carried out over CeX₁₀ catalyst.

Mass transfer considerations: In any kinetic study, the resistances due to film (external) and pore (internal) diffusion must be minimized in order to propose an intrinsic rate. For the estimation of external diffusion effects, two series of runs were taken with 0.03 and 0.05 kg of catalyst.

Conditions: Benzene/EtOH, 3:1; temperature, 513K; W/F, 19.47 kg h kgmol⁻¹; pressure, 1 atm.

Keeping W/F ratio constant, each series with a constant benzene to ethyl alcohol feed mole ratio of 3:1 at a fixed temperature and pressure of 513 K and 1 atm, conversion of benzene remains same in both the cases showing complete absence of external diffusion. A fixed nitrogen-to-feed (N₂/F) molar ratio of 0.33 was used in all the runs. The external mass transfer resistance is, therefore, negligible. Since, the mass transfer is a function

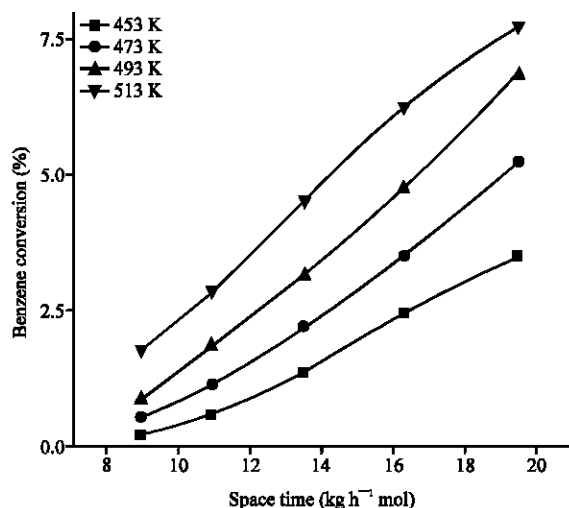
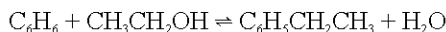


Fig. 4: Effect of space time on benzene conversion at different temperatures

of rate of flow of feed, it can be concluded that above a minimum value of feed flow rate the external mass transfer effect is negligible. The minimum flow rate of feed employed was $1.5 \times 10^{-4} \text{ m}^3 \text{ h}^{-1}$ corresponding to W/F ratio of $19.47 \text{ kg h kg mole}^{-1}$ of liquid feed and for all other investigations a flow rate of feed above this minimum was used. Kinetic studies were carried out in such a reaction condition in which there is no effect of external and internal diffusion.

Kinetic modeling: In the absence of pore diffusional resistance, a mechanism involving chemisorption and surface reaction will control the rate of catalytic reaction.

In the present study, the cases involving chemisorption as rate controlling step were not considered. Hence only those cases where surface reaction is rate controlling were taken for investigation. Kinetic runs were carried out at four different temperatures, viz., 453, 473, 493 and 513 K. At each temperature, W/F was varied by changing the liquid feed rate. The effect of space-time (W/F) on benzene conversion at three different temperatures is presented in Fig. 4. It was observed that benzene conversion increases with an increase in space-time at all temperatures. Different models based on Langmuir-Hinshelwood mechanisms were formulated using the approach suggested by Hougen and Watson. In this, the various mechanisms, which might control the reaction, were based on single site and dual site. Alkylation of benzene with ethyl alcohol to form ethylbenzene and water can be represented by the following reaction:



The possible isothermal rate equations for the above reaction based on single and dual site mechanisms for the case where surface reaction is the rate controlling are presented below. P_B, P_E, P_{EB} are partial pressure of component benzene, ethanol and ethyl benzene, respectively. k is the kinetic constant, kgmol/kg.atm.h , K_B, K_E, K_{EB}, K_w are the adsorption constant for benzene, ethanol, ethyl benzene and water, respectively.

Single-site mechanism:

- Model 1: E in gas phase

$$r_B = \frac{kK_E[P_E P_B - (P_{EB} P_w / K)]}{1 + K_B P_B + K_{EB} P_{EB} + K_w P_w} \tag{1}$$

- Model 2: B in gas phase:

$$r_B = \frac{kK_E[P_E P_B - (P_{EB} P_w / K)]}{1 + K_E P_E + K_{EB} P_{EB} + K_w P_w} \tag{2}$$

Dual-site mechanism:

- Model 3: Both B and E adsorbed

$$r_B = \frac{kK_B K_E [P_E P_B - (P_{EB} P_w / K)]}{Z^2} \tag{3}$$

where, $Z = 1 + K_B P_B + K_E P_E + K_{EB} P_{EB} + K_w P_w$ Model 1 and 2 were rejected on the basis of negative adsorption constants and improper trends of these constants with temperature. For each temperature, the space-time-conversion data have been analyzed and the rates of reaction were obtained by differential analysis of the plug flow reactor equation.

$$r_{obs} = \frac{dX_B}{d(W/F_{B0})} \tag{4}$$

where, W is mass of the catalyst, kg . F_{B0} is the total feed rate, kg mol h^{-1} . Since, the conversion of benzene is small (7.85%), the reverse reaction is neglected. A mathematical fit for Model 3 was performed as follow:

Rate of disappearance of benzene:

$$r_B = \frac{kK_B K_E P_B P_E}{(1 + K_B P_B + K_E P_E + K_{EB} P_{EB})^2} \tag{5}$$

The partial pressures in the above equation are related to the conversions and total pressure P by the relationships:

$$p_B = (1 - X_B) P/2 \quad (6)$$

$$p_E = (0.5 - X_B) P/2 \quad (7)$$

$$p_{EB} = X_B P/2 \quad (8)$$

Therefore:

$$r_B = \frac{kK_B K_E (1 - X_B) X (0.5 - X_B) P^2 / 2^2}{[1 + K_B (1 - X_B) P / 2 + K_E (0.5 - X_B) P / 2 + K_{EB} X_B P / 2]^2} \quad (9)$$

The above rate equation contains four unknown parameters, viz., k, K_B, K_E and K_{EB}. These parameters were estimated by treating each temperature data separately. As the rate equation is non-linear with respect to unknown parameters, a non-linear regression program based on Marquardt's algorithm (Marquardt, 1963) was used to obtain a mathematical fit for the above rate equation by minimizing the objective function for the residual sum of squares given by the equation:

$$f = \sum_{i=1}^n [(X_{pred})_i - (X_{exp})_i]^2 \quad (10)$$

The initial rate estimates of the various constants of the rate expression were made from the composition pattern of the product stream (p_B, p_E, p_{EB}). The kinetic and adsorption constants estimated by non-linear regression. It was observed that with increase in temperature the kinetic constants increase, which is the right trend for these parameters and the adsorption constants show a decreasing trend with increase in temperature as expected. The kinetic constants evaluated and tabulated at various temperatures were used to determine the activation energy and frequency factor using Arrhenius relationship, $k = k_0 \exp(-E_a/RT)$. The apparent activation energy was calculated to be 63.23 kJ mol⁻¹ and the frequency factors k₀ as 3.83x10⁵ kgmol/(kg.atm.h). Allakhverdieva *et al.* (1968) obtained a value of 50-67 kJ mo on CaY and LaY for isopropylation of benzene. Bhat *et al.* (1998) also reported similar values of activation energy and frequency factor for alkylation of toluene with methanol over HZSM-8 zeolite. The experimentally observed rate of reaction and the theoretically predicted rate values at the four temperatures are plotted in Fig. 4. A fairly good correlation was observed in Fig. 5 between the observed

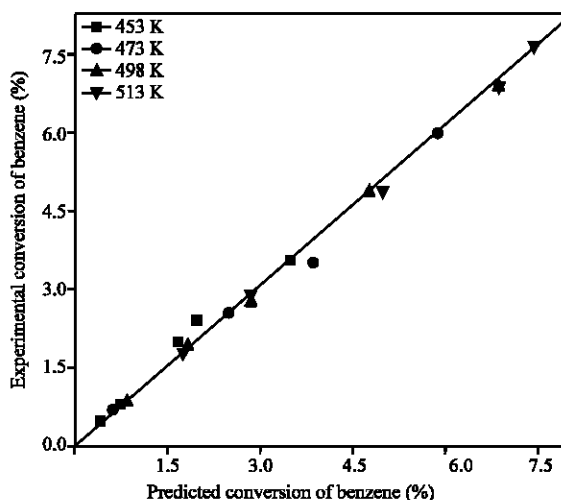


Fig. 5: Experimental vs. predicted benzene conversions

and predicted benzene conversions. Thus the proposed kinetic model fits well into the experimental observations.

CONCLUSION

An attempt was made to systematically study the effect of acidity of modified NaX zeolite in alkylation of benzene with ethanol and the kinetic study of the ethylation reaction. Exchanging sodium ions of the zeolite by cerium ions was found to enhance its acidity and activity in benzene ethylation. A L-H-H-W surface reaction model with benzene and ethyl alcohol adsorbed on two active sites of the catalyst (before reacting with each other) agreed well with the experimental data in the external and macropore diffusional resistances free regime. A nonlinear regression method was used to estimate the kinetic parameters of the rate equation. The apparent activation energy and the frequency factor were computed from the Arrhenius equation and they compared well with the values reported by earlier workers on similar alkylations on large pore zeolites.

ACKNOWLEDGMENTS

One of the authors, Sanghamitra Barman is thankful to the Council of Scientific and Industrial Research (CSIR), New Delhi, India for the award of senior research fellowship during the tenure of this study.

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