Kinetic study of alkylation of benzene with ethanol over bimetallic modified HZSM-5 zeolite catalyst and effects of percentage metal loading

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Abstract Alkylation of benzene with ethanol was analyzed using shape selective boron–magnesium bimetallic HZSM-5 (Si/Al = 90) zeolite catalyst. The alkylation of benzene with ethanol (2:1 by volume) produces ethylbenzene as primary product and others like 1, 2-Diethylbenzene, 1, 4-Diethylbenzene, and xylene mixtures as secondary products. The physiochemical properties of catalyst were characterized by XRD, BET, TGA, FTIR, NH\textsubscript{3}-TPD, and FE-SEM. The feed and products were analyzed by gas chromatography and mass spectroscopy. B–Mg bimetallic catalysts supported on HZSM-5 zeolite catalyst with SAR = 90 were synthesized by the incipient wetness impregnation method and examined for alkylation of benzene with ethanol. Total metal loading of 5, 10, and 15% was used for catalyst synthesis. The highest selectivity of ethylbenzene (76.22%) was obtained by (Mg + B)-15%-HZSM-5 and the lowest ethylbenzene selectivity (49.15%) was obtained by (Mg + B)-5%-HZSM-5 using 2:1 benzene-to-ethanol ratio by volume. A reaction scheme with three parallel routes leading to the formation of ethylbenzene, diethylbenzene, and triethylbenzene was considered for the kinetic study. The kinetic parameters were determined using Langmuir–Hinshelwood–Hougen–Watson (LHHW)-type kinetic model. LHHW model could satisfactorily correlate the rate data and this model gives good fit between the experimental and calculated data.

Graphical abstract Possible mechanism for benzene alkylation with ethanol to form ethylbenzene.

Keywords Alkylation, HZSM-5, Benzene, Ethanol, Ethylbenzene

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Introduction

Porous solids with pores of the size of molecular dimensions, 0.3–2.0 nm in diameter are called molecular sieves. Examples include zeolites, carbons, glasses, and oxides. Some are crystalline with a uniform pore size and more described in detail by their crystal structure, for example, zeolites.\textsuperscript{1}

Zeolites are so special when compared to other crystalline inorganic oxide materials due to a combination of the following properties: the microporous character with uniform pore dimensions, allowing certain hydrocarbon molecules to enter the crystals while rejecting others based on too large a molecular size, the ion-exchange properties which allow to perform all sorts of ion exchange reactions, the ability to develop internal acidity which makes the zeolites interesting materials for catalyzing organic reactions, and the high thermal stability of the zeolites.\textsuperscript{2}

According to International Zeolite Association (2014), until now, there are 218 zeolite framework type codes that have been discovered. Worldwide consumption of zeolites (natural and synthetic) is estimated to be about 5 million tons per year. The annual market for synthetic zeolites and molecular sieves was developed vastly to 1,800,000 ton worldwide in 2008.\textsuperscript{3}

Alkylation of benzene is a vital reaction in the petrochemical industry. Benzene alkylation technologies offer improvements in octane number and gasoline volume. Ethylbenzene, diethylbenzene, toluene, and xylenes are important raw materials for many intermediates of commodity petrochemicals and valuable fine chemicals.\textsuperscript{4}

Alkylation of benzene with ethanol was analyzed using shape selective boron–magnesium bimetallic HZSM-5 (Si/Al = 90) zeolite catalyst. The alkylation of benzene with ethanol (2:1 by volume) produces ethylbenzene as primary product and others like 1, 2-Diethylbenzene, 1, 4-Diethylbenzene, and xylene mixtures as secondary products. The physiochemical properties of catalyst were characterized by XRD, BET, TGA, FTIR, NH\textsubscript{3}-TPD, and FE-SEM. The feed and products were analyzed by gas chromatography and mass spectroscopy. B–Mg bimetallic catalysts supported on HZSM-5 zeolite catalyst with SAR = 90 were synthesized by the incipient wetness impregnation method and examined for alkylation of benzene with ethanol. Total metal loading of 5, 10, and 15% was used for catalyst synthesis. The highest selectivity of ethylbenzene (76.22%) was obtained by (Mg + B)-15%-HZSM-5 and the lowest ethylbenzene selectivity (49.15%) was obtained by (Mg + B)-5%-HZSM-5 using 2:1 benzene-to-ethanol ratio by volume. A reaction scheme with three parallel routes leading to the formation of ethylbenzene, diethylbenzene, and triethylbenzene was considered for the kinetic study. The kinetic parameters were determined using Langmuir–Hinshelwood–Hougen–Watson (LHHW)-type kinetic model. LHHW model could satisfactorily correlate the rate data and this model gives good fit between the experimental and calculated data.

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Ethylbenzene (EB), which is one of the most important products used as the chemical intermediate, is the main feedstock for the synthesis of styrene which is then polymerized into polystyrene, a common plastic material.\textsuperscript{4} Ethylbenzene is also used in the chemical industry in the manufacture of acetophenone, cellulose acetate, diethylbenzene (DEB), ethyl anthraquinone, ethylbenzene sulfonic acids, propylene oxide, and α-methylbenzyl alcohol.\textsuperscript{5} Additionally it is used as a solvent, a constituent of asphalt and of naphtha, and in fuels. Ethylbenzene and xylene mixtures are used in the paint industry and in the production of pesticides in agriculture.\textsuperscript{5}
Several researchers have proposed the alternative catalytic reaction pathways for the production of ethylbenzene. The catalytic reaction which uses ethanol for benzene alkylation, instead of ethene, would eliminate the ethene production step and, therefore, leading to the commercial and environmental benefits in the ethylbenzene manufacturing. In addition to the intrinsic scientific interest, the direct use of ethanol (instead of ethene) in the manufacture of ethylbenzene also has economic significance in those countries like Brazil and India, where biomass-derived alcohol is an additional feedstock for the manufacture of chemicals (see Fig. 1).

Several studies have been reported regarding benzene alkylation using unmodified zeolites like HZSM-5, Beta, HY, mordenite, TNU-9, SSZ-33, ZSM-12, MCM-22, and ITQ-22 as well as HZSM-5 modified with phosphorous and boron. Venuto et al. had shown that although Linde-type X and Y zeolites exchanged with rare earth ions catalyze the alkylation of benzene with ethene, the catalyst aging was severe leading to catalyst deactivation in a few hours. Junhui Li et al. had performed alkylation of benzene with ethanol for the synthesis of ethylbenzene over parent zeolites and zeolites modified with La2O3, such as HMC-22, HBeta, and nano HZSM-5.

In the reaction of converting benzene to ethylbenzene, HZSM-5 zeolite has been used as a catalyst. It is well known that the alkylation reaction of benzene in the presence of an acid catalyst belongs to a carbenium ion type mechanism. The alkylation of benzene with ethanol produces ethyl benzene as primary product and others like diethyl benzene and xylene mixtures as secondary products (see Fig. 2). This research focused on the kinetic study of alkylation of benzene with ethanol over bimetallic-modified HZSM-5 zeolite catalyst and effects of percentage metal loading.

**Experimental**

**Materials**

The chemicals and gases used in the experiments were obtained from different manufacturers and suppliers. ZSM-5 zeolite in protonic and powder form with SAR 90 was obtained from Sud-Chemie India Pvt. Ltd. Benzene used in the experiments was 99% pure. Boric acid (99.5% pure) and benzene for the present study were obtained from RFCL limited, New Delhi, India. Pure ethanol (99.9%) was supplied by Merck KGaA, Germany. Magnesium nitrate (99% pure) was supplied by HiMedia laboratories Pvt. Ltd. Mumbai, India.

**Catalyst preparation**

HZSM-5 SAR = 90 obtained from Sud-Chemie India Pvt. Ltd was in protonic form so that no further transformation activities were done except catalyst was calcined at 550 °C for 5 h to be activated. Boron–magnesium bimetallic catalysts were prepared by the incipient wetness impregnation method. In this method, desired amount of metal precursors (H3BO3 and Mg(NO3)2·6H2O) were dissolved in deionized water and calculated amount of HZSM-5 zeolite catalyst was added to this solution under stirring. Total metal loading for bimetallic catalysts was 5, 10, and 15 wt%. The zeolite powder so obtained was pelletized at 10 tonne/cm2 pressure and broken into small pieces in the size range of 0.3–0.5 mm. The fraction in this size range was used in the reactor for the activity test runs.

**Experimental setup**

The catalytic experiments were carried out in a fixed bed; continuous down flow tubular quartz (0.6-cm i.D and 66-cm long) reactor placed inside a microprocessor-controlled furnace (Metrex Scientific Instruments Pvt. Ltd, New Delhi) which was preceded by a pre-heater and followed by a condenser. The same reactor tube was used in all the experiments. In a typical run, about 0.7 g of catalyst (which occupied 6 cm height of the reactor) was charged into the reactor and the reaction was carried out at atmospheric pressure using bimetallic HZSM-5 catalyst. The catalysts activated for one hour in an atmosphere of nitrogen before the experimental runs were started. The benzene ethanol mixture of 2:1 ratio introduced with the help of a metering pump at rate of 0.4 ml/min and vaporized in the pre-heater before contacting the catalyst. The reactant vapors along with nitrogen entered the reactor, which was electrically heated. The flow rate of the nitrogen carrier gas was 0.5 liters per minute. The products vapors, along with unreacted reactants, were condensed in the condenser and the liquid samples collected were analyzed in a gas chromatograph and mass spectroscopy with a 30 m × 0.32 mm (0.25 μm film thickness) Elite-1 capillary column (Perkin Elmer) using a flame ionization detector (FID). The program used was as follows. Initial oven temperature was 70 °C then held for 2 min. After that the temperature was increased to 200 °C with a ramp rate of 10 °C/min. Again it stayed at 200 °C for 1 min. The Detector and injection temperature was 250 °C.
Flow rate of air, hydrogen, and nitrogen were 450, 45, and 45 ml/min, respectively. Nitrogen was used as carrier gas and the split ratio was 1:50. From gas chromatography results, the selectivity and yield of ethylbenzene in the product were calculated. The conversion of benzene was also noted for bimetallic HZSM-5 catalysts (Fig. 3).

Catalyst characterization

The catalysts were characterized by various methods including surface area measurement, X-ray diffraction, temperature-programmed desorption, inductive-coupled plasma-mass spectroscopy, scanning electron microscopy, and transmission electron microscopy.

\( \text{N}_2 \) adsorption–desorption isotherm measurements were performed at –196 °C using a Micrometrics Accelerated Surface Area and Porosimetry (ASAP-2020) system. Prior to the analysis, the samples were degassed at 250 °C for 8 h under vacuum. The surface area of all the samples was analyzed employing the multi point Brunauer–Emmett–Teller (BET) method using adsorption data at the relative pressure \( (P/P_0) \) range of 0.05–0.3. Pore size distribution was determined using the Barret–Joyner–Halenda (BJH) method considering the desorption branch.

X-ray diffraction (XRD) analysis was performed in order to determine the phase structure of the catalyst and crystallinity. The spectra were recorded with a Bruker AXS D8 advance diffractometer using Cu-K\( \alpha \) monochromatized radiation source \( (\lambda = 1.5418 \text{ Å}) \), Ni filter, and 40 kv at the two theta interval of 5–50° with scan speed of 1°/min. The average crystallite size of the catalysts was determined using Scherrer formula \( D = 0.90 \lambda /\beta \cos \theta \), where \( \beta \) is the full width at half-maximum height.
Effect of physicochemical properties

X-ray diffraction

XRD patterns of magnesium–boron bimetallic HZSM-5 zeolite catalysts are given in Fig. 4. X-ray powder diffraction was employed to determine the value of relative crystallinity (RC). The commercial zeolite, HZSM-5 was assumed to have 100% crystallinity. The determination of the value was based on the area of the characteristic peaks in the 2θ range from 22.5° to 25°. XRD analysis was carried out using powder diffractometer (Bruker D8) at Institute Instrumentation Centre (IIC), Indian Institute of Technology Roorkee. Cu-Kα (λ = 1.5417 Å, 40 kv and 30 mA) was used as anode material and the range of scanning angle (2θ) was kept between 5° and 50° with scan speed.
Thermogravimetric analysis

Thermogravimetric analysis of HZSM-5 modified by bimetallic magnesium–boron is shown in Fig. 5. Thermogravimetric analysis was conducted in order to determine the thermal stability of the zeolite framework and weight loss occurring from zeolite lattice during heating. TGA was conducted on SII 6300 EXSTAR instrument using air as carrier gas at 200 ml/min on a 10 mg of sample. Figure 5 presents the TGA of modified and unmodified HZSM-5 heated from ambient temperature to 1000 °C in temperature progression of 10 °C/min. The portion of the curve up to 100 °C is normally linked with the weight loss due to moisture content of the catalyst, whereas, the portion of the curve from 100 to 1000 °C is assigned to the weight loss due to the removal of hydrocarbon, moisture contained inside the pores, and coke formation. From the experimental investigation, it is seen that high percent weight loss is demonstrated by magnesium-boron modified catalysts. As the amount of percent metal loading is increased the weight lost by the catalysts is also increased, particularly at higher temperatures as shown in the Table 2.

FTIR analysis

Infrared spectra were obtained at 4 cm⁻¹ resolution on Nicolet 6700 series FTIR Spectrometer. The infrared cell used was fitted with KBr windows. A sample of the zeolite powder was
of HZSM-5 has decreased after modification with bimetallic magnesium–boron. This may be due to the deposition of bimetals on the outer surface of the catalyst deactivating the active sites. A significant change in acidic sites was observed for (Mg + B)-15%-HZSM-5 zeolite catalysts.

Strong acid sites are the main cause for alkylation reaction. If they exist on the surface of catalysts in large quantity they facilitate further alkylation of ethylbenzene with ethanol to diethylbenzene and other undesired products. So that it is desirable to reduce the amount of strong acid sites. There is a shift in peak temperature for curve (b) (Fig. 7) due to reduction in strong acidic sites and emerging of weak acid sites due to metal loading (Table 3).

**Ammonia temperature-programmed desorption (NH₃-TPD)**

The ammonia temperature-programmed desorption was conducted according to the procedure stated in section Catalyst characterization. From the NH₃-TPD experiments (Fig. 7), it could be concluded that two types of acid sites were present in H-ZSM-5: weak acid sites corresponding to desorption at low temperature and strong acid sites corresponding to desorption at high temperature. It was observed that the acidity of HZSM-5 has decreased after modification with bimetallic magnesium–boron. This may be due to the deposition of bimetals on the outer surface of the catalyst deactivating the active sites. A significant change in acidic sites was observed for (Mg + B)-15%-HZSM-5 zeolite catalysts.

**Characterization**

**Field emission scanning electron microscope**

The morphology of the zeolite samples was evaluated by Field Emission Scanning Electron Microscope (FE-SEM) using ULTRA plus. Scanning Electron Microscopic images of the samples are shown in Fig. 8.

**BET surface area**

Table 4 shows the surface area and pore volume of unmodified and modified HZSM-5 zeolite catalysts. The surface area of HZSM-5 (SAR = 90) was 347 m²/g. It can be found from Table 4 that the surface area of support was reduced significantly after metal impregnation. Among the modified support catalysts, the surface area of (Mg + B)-5%-HZSM-5 catalyst was highest (318 m²/g) and the surface area of (Mg + B)-15%-HZSM-5 catalyst was lowest (283 m²/g).
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ethylbenzene, p-xylene, m-xylene, o-xylene, and diethylbenzene. The gaseous products contained negligible amount of hydrocarbon gases (ethane, methane, ethylene, etc.).

The following equations were used to check the activity of the catalysts:

\[
\text{Benzene conversion (\% \(X_B\)) = \frac{\text{Moles of benzene converted}}{\text{Moles of benzene in the feed}} \times 100}
\]

\[
\text{Ethylbenzene yield (\% \(Y_{EB}\)) = \frac{\text{Moles of ethylbenzene obtained}}{\text{Moles of benzene converted}} \times 100}
\]

\[
\text{Ethylbenzene selectivity (\% \(S_{EB}\)) = \frac{\text{Moles of ethylbenzene(desired product) formed}}{\text{Moles of all products formed}} \times 100}
\]

Performance of bimetallic and unmodified HZSM-5 (SAR = 90) catalyst

In the present study, the performances of HZSM-5 catalyst with a silicon-to-aluminum ratio of 90 for the alkylation reaction of benzene with ethanol were studied. Experiments were carried out in a fixed catalytic bed down flow reactor at a constant feed (benzene and ethanol mixture 2:1 by volume) rate of 0.4 ml/min and a carrier gas (N\(_2\)) flow 0.5 liters per minute (lpm). The WHSV of benzene and ethanol mixture as feed was 32.6 h\(^{-1}\). Nitrogen was used as carrier gas to activate the catalyst. The products of the reaction were analyzed by gas chromatograph. Liquid products contained benzene, ethanol, toluene, catalyst was the lowest (268 m\(^2\)/g). Total pore volume of the unmodified HZSM-5 zeolite catalysts was also reduced after modification. This may be due to the deposition of metal cations used for modification.

**Table 4** BET surface area of different types of HZSM-5 (SAR = 90) catalysts

| Type of catalyst                  | BET surface area (m\(^2\)/g) | External surface area (m\(^2\)/g) | Total pore volume (cm\(^3\)/g) | Average pore width (4V/A by BET) (Å) |
|----------------------------------|------------------------------|----------------------------------|-------------------------------|-----------------------------------|
| Unloaded HZSM-5                 | 347                          | 144                              | 0.34                          | 24.15                             |
| (Mg+B)-5%-HZSM-5                | 318                          | 125                              | 0.30                          | 24.44                             |
| (Mg+B)-10%-HZSM-5               | 285                          | 108                              | 0.21                          | 24.53                             |
| (Mg+B)-15%-HZSM-5               | 268                          | 87                               | 0.19                          | 24.70                             |

Figure 8  Fe-SEM image of bimetallic and unmodified HZSM-5 zeolite catalyst

![Fe-SEM image of bimetallic and unmodified HZSM-5 zeolite catalyst](image-url)
facilitates further reactions. The highest conversion of benzene was under taken by unmodified HZSM-5. When we compare bimetallic-modified HZSM-5 zeolite catalysts, the highest metal loading gave best result in terms of selectivity of ethylbenzene while the lowest metal loading is best in terms of yield of ethylbenzene and benzene conversion. These results are related with the physicochemical properties of the catalysts such as pore size and surface acidity. Pore size, surface area, and total acidity of catalysts decreased as percentage metal loading increased.

**Kinetic study**

This section discusses the kinetic study of alkylation reaction of benzene with ethanol over (B–Mg)-15%-HZSM-5 zeolite catalyst. The kinetic experiments were carried out in the presence of (B–Mg)-15%-HZSM-5 catalyst since it was the most active and selective catalyst among all the catalysts examined. The kinetic experiments of the alkylation of benzene with ethanol were carried out in fixed bed tubular reactor in the temperature range from 300 to 500 °C and atmospheric pressure. The kinetic study was done using different weight hour space velocities from 5 to 32.6 h⁻¹. Nitrogen to feed ratio 4.2 and feed ratio (benzene to ethanol) 2:1 were used. The reaction data were used to calculate the initial reaction rate and activation energy. The kinetic model used to fit the data was the Langmuir–Hinshelwood–Hougen–Watson (LHHW) model.

**Kinetic model development**

*Langmuir–Hinshelwood–Hougen–Watson (LHHW) model*

Reaction mechanism for alkylation of benzene with ethanol can be represented by the following steps which are used to derive the rate equations.

**Step 1: Adsorption**

Adsorption of ethanol (E) on the surface of vacant sites (S):

\[
S + E \rightarrow ES
\]

From our experimental investigation, we were observed that when HZSM-5 zeolite catalyst modified by different percentage metal loading, it affects performance of the catalysts such as yield, selectivity, and conversion. From our previous work, we had seen that bimetallic boron–magnesium modified is better than monometallic either boron or magnesium-modified HZSM-5. For this reason, this work focuses on the kinetic study of bimetallic-modified HZSM-5 and effect of percentage metal loading. The performances of bimetallic modified and unmodified HZSM-5 catalyst for a benzene-to-ethanol ratio 2:1 by volume are shown in Figs. 9–11. It was observed that the highest yield of ethylbenzene (45.03%) was obtained at 450 °C using unmodified HZSM-5. However, the highest ethylbenzene selectivity (76.22%) was observed when the catalyst was modified with (Mg + B)-15%-HZSM-5. This happened due to decrease in pore size and surface acidity of the catalyst which
From equation (6–13), the rate equations can be represented as

\[ (-r_1) = k_1 \left( C_{E,S} - \frac{C_{E,B,S}}{K_1} \right), \quad K_1 = \frac{k_1}{k_1} \]

\[ (-r_2) = k_2 \left( C_{B,S} - \frac{C_{B,E,S}}{K_2} \right), \quad K_2 = \frac{k_2}{k_2} \]

\[ (-r_3) = k_3 \left( C_{B,S}C_{E,S} - \frac{C_{B,S}C_{W,S}}{K_3} \right), \quad K_3 = \frac{k_3}{k_3} \]

\[ (-r_4) = k_4 \left( C_{E,S} - \frac{C_{E,B,S}C_{W,S}}{K_4} \right), \quad K_4 = \frac{k_4}{k_4} \]

\[ (-r_5) = k_5 \left( C_{DEB,S} - \frac{C_{DEB,S}C_{W,S}}{K_5} \right), \quad K_5 = \frac{k_5}{k_5} \]

\[ (-r_6) = k_6 \left( C_{EBS} - \frac{C_{EBS}C_{S}}{K_6} \right), \quad K_6 = \frac{k_6}{k_6} \]

where \( K_1, K_2, K_3, K_4, K_5, \) and \( K_6 \) are the equilibrium constants for respective reactions.

It is assumed that the surface reaction is the rate controlling step, and then the rate of surface reactions are given as follows,

From equation (16),

\[ (-r_1) = k_1 C_{E,S} C_{B,S} \]

From equation (17),

\[ (-r_4) = k_4 C_{E,S} C_{E,S} \]

From equation (18),

\[ (-r_5) = k_5 C_{DEB,S} C_{E,S} \]

If the adsorption and desorption steps are very fast, then the concentrations of adsorbed species can be calculated by assuming that the adsorption and desorption steps are at equilibrium. The concentration of adsorbed species can be obtained as follows:

From equation (14),

\[ \frac{r_1}{k_1} = 0, \quad C_{E,S} = K_1 C_{E,S} \]

From equation (15),

\[ \frac{r_2}{k_2} = 0, \quad C_{B,S} = K_2 C_{B,S} \]

From equation (19),

\[ \frac{r_5}{k_5} = 0, \quad C_{DEB,S} = \frac{C_{DEB,S} C_{E,S}}{K_4} \]

From equation (20),

\[ \frac{r_6}{k_6} = 0, \quad C_{EBS} = \frac{C_{EBS} C_{S}}{K_6} \]

On substituting these values in surface reaction rates

\[ (-r_1) = k_1 K_2 K_4 C_{E,B,S} C_{B,S} \]

\[ (-r_4) = k_4 K_2 K_3 C_{E,B,S} C_{E,S} \]

\[ (-r_5) = k_5 K_2 K_4 C_{E,B,S} C_{E,S} \]

Now, the total concentration of active sites on the surface, \( C_{A,S} \), can be expressed as the sum of concentration of all sites on
which reactants and products are adsorbed and the concentration of vacant sites which yields,
\[ C_v = C_s + C_{E_b s} + C_{E_b s} + C_{DEB s} + C_{TEB s} \]  

(33)

\[ C_s = \frac{C_T}{1 + K_1 C_E + K_2 C_B + \frac{C_{ads}}{K_s} + \frac{C_{ads}}{K_s}} \]  

(34)

Substituting equation (34) into equation (30–32), then
\[ (r_3) = \frac{k_1' C_I C_B}{\left(1 + K_1 C_E + K_2 C_B + \frac{C_{ads}}{K_s} + \frac{C_{ads}}{K_s}\right)^2} \]  

(35)

\[ k_1' = \frac{k_1 K_2 C_I}{K_6} \]  

\[ (r_4) = \frac{k_1' C_I C_{DEB}}{\left(1 + K_1 C_E + K_2 C_B + \frac{C_{ads}}{K_s} + \frac{C_{ads}}{K_s}\right)^2} \]  

(36)

\[ k_1' = \frac{k_1 K_2 C_I}{K_7} \]  

\[ (r_5) = \frac{k_1' C_I C_B}{\left(1 + K_1 C_E + K_2 C_B + \frac{C_{ads}}{K_s} + \frac{C_{ads}}{K_s}\right)^2} \]  

(37)

It is important to note that the adsorption of water is negligible. Hence, \( K_6 \) equals to zero in the above surface coverage expressions.

For each temperature, the space–time-conversion data have been analyzed and the rates of reaction were obtained by the differential analysis of the plug flow reactor equation:
\[ r_{obs} = \frac{dX_B}{(W/F_{I0})} \]  

(38)

\[ \frac{dX_B}{dZ} = (r_A)(\text{bulk density}) \frac{F_{I0}}{F_{I0}} \]  

(39)

where \( r_{obs} \) = experimentally observed rate of reaction of B, \( W \) = mass of the catalyst, B = benzene, \( X_p \) = fractional benzene conversion, \( F_{I0} \) = feed rate of benzene, \( z \) = bed length, and \( A \) = bed cross sectional area.

The intrinsic rate constant can be expressed according to the Arrhenius equation:
\[ k = k_o \exp \left(\frac{-E}{RT}\right) \]  

(40)

Conventionally, the temperature dependence relations of the adsorption equilibrium constants can be expressed according to the following thermodynamic relations:

\[ K_i = \exp \left(\frac{-\Delta G_{ads,i}^o}{RT}\right) \]  

(41)

where \( \Delta G_{ads,i}^o \) is the Gibbs free energy for adsorption of species i under standard conditions (298 K and 1 atm) which is further related to the change of enthalpy \( \Delta H_{ ads,i}^o \) and change of entropy \( \Delta S_{ads,i}^o \) of adsorption as follows:
\[ \Delta G_{ads,i}^o = \Delta H_{ads,i}^o - T \Delta S_{ads,i}^o \]  

(42)

From equations (41) and (42),
\[ K_i = \exp \left(\frac{\Delta S_{ads,i}^o}{R} - \frac{\Delta H_{ads,i}^o}{RT}\right) \]  

(43)

Alternatively, the above equation (43) can be represented with the centered temperature form as:
\[ K_i = \exp \left(D_i - F_i \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \]  

(44)

where \( D = \frac{\Delta S_{ads}}{R} \) and \( F = \frac{\Delta H_{ads}}{RT} \)

If we assume that the adsorption of water and nitrogen does not compete with the adsorption of hydrocarbons, the influence of water and nitrogen adsorption could be neglected. With these assumptions, the rate equations, equations (35) and (36) become
\[ (r_3) = \frac{k_1' p_B p_B}{\left(1 + K_1 p_E + K_2 p_B + \frac{p_{ads}}{K_s} + \frac{p_{ads}}{K_s}\right)^2} \]  

(45)

\[ k_1' = k_1 K_2 C_I \]  

\[ (r_4) = \frac{k_1' p_B p_{EB}}{\left(1 + K_1 p_E + K_2 p_B + \frac{p_{ads}}{K_s} + \frac{p_{ads}}{K_s}\right)^2} \]  

(46)

\[ k_1' = k_1 K_2 C_I \]  

\[ (r_5) = \frac{k_1' p_B p_{EB}}{\left(1 + K_1 p_E + K_2 p_B + \frac{p_{ads}}{K_s} + \frac{p_{ads}}{K_s}\right)^2} \]  

(47)

The partial pressures in the above equations are related to the conversion and total pressure \( P \) by the following relationship:
\[ P_B = \frac{(1 - x_B)P}{(7.8 + x_B)} \]  

(48)

\[ P_E = \frac{(0.5 - x_B)P}{(7.8 + x_B)} \]  

(49)

\[ P_{EB} = \frac{(x_B)P}{(7.8 + x_B)} \]  

(50)
Table 5  Estimated kinetic and adsorption constants

| Constants | T = 350 °C | T = 400 °C | T = 450 °C |
|-----------|------------|------------|------------|
| $k'_1$ (kg mol/kg cat h) | 11.23 | 13.12 | 15.00 |
| $k'_2$ (kg mol/kg cat h) | 25.60 | 30.25 | 35.10 |
| $K_1$ (L/mol) | 0.42 | 0.34 | 0.23 |
| $K_2$ (L/mol) | 0.58 | 0.49 | 0.37 |
| $K'_3$ (L/mol) | 67.00 | 63.00 | 60.00 |
| $K'_4$ (L/mol) | 49.00 | 47.00 | 44.00 |

Table 6  Estimated parameter values

| Kinetic parameter | Activation energy, $E_a$ (kJ/mol) | Pre-exponential factor, $k_o$ (kg mol/kg cat h) |
|-------------------|----------------------------------|-----------------------------------------------|
| $k'_1$ | 14.3 | 169.85 |
| $k'_2$ | 15.4 | 479.19 |
| $K'_3$ | 22.68 | 5.36 x 10^{-3} |
| $K'_4$ | 165.6 | 2.36 x 10^{-2} |
| $K'_5$ | 4.49 | 28.02 |
| $K'_6$ | 21.44 | 1.12 x 10^3 |

Conclusions

From the present study on the performance of magnesium–boron-modified HZSM-5 (SAR = 90) catalysts and its kinetic study, the following conclusions can be made:

1. During alkylation of benzene with ethanol using either modified or unmodified HZSM-5 catalysts, ethylbenzene was the primary product, while diethylbenzene, triethylbenzene, toluene, and xylene mixtures were also observed in the product.

2. For boron–magnesium bimetallic-modified HZSM-5, the highest selectivity of ethylbenzene (76.22%) was obtained by (Mg + B)-15%-HZSM-5 and the lowest ethylbenzene selectivity (49.15%) was obtained by (Mg + B)-5%-HZSM-5 using 2:1 benzene-to-ethanol ratio by volume.

3. The highest selectivity of ethylbenzene was obtained by bimetallic modified HZSM-5 due to synergistic effect.

\[
(-r_y) = \frac{k'_1(0.5 - x_y)(1 - x_y)P^2/(7.8 + x_y)}{\left(1 + K_1(0.5 - x_y) + K_2(1 - x_y) + \frac{2a}{K_2} + \frac{2b}{K_1} \right) \left(P/(7.8 + x_y) \right)}^{k'}
\]

\[
(-r_y) = \frac{k'_2(0.5 - 0.5x_y)(1 - x_y)P^2/(7.8 + x_y)}{\left(1 + K_1(0.5 - x_y) + K_2(1 - x_y) + \frac{2a}{K_2} + \frac{2b}{K_1} \right) \left(P/(7.8 + x_y) \right)}^{k''}
\]

\[
k'' = \frac{kK_C}{k'}
\]

4. A reaction scheme with three parallel routes leading to the formations of ethylbenzene, diethylbenzene, and triethylbenzene considered for the kinetic study. The kinetic parameters were determined using LLHHW-type kinetic models. LLHHW model could satisfactorily correlate the rate data and this model gives good fit between the experimental and calculated data.

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