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A comparative study of catalytic performance of rare earth metal-modified beta zeolites for synthesis of cymene

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Abstract A series of zeolite (LaB, CeB, and PrB) containing rare earth metals lanthanum (La), cerium (Ce), and praseodymium (Pr) were used for transalkylation reaction. The modified beta zeolites were characterized by EDS, XRD, BET, FTIR, and TPD. The surface area and acidities of the zeolite samples modified with various rare earth metals are considerably different. The effect of various process parameters like metal loading (2-10 wt%), catalyst loading (1.44-8.63 w/w%), temperature (448-573 K), reactant ratio 1-15, and space time (3.2-9.29 kg h/kmol) on the conversion of reactant and selectivity of product was studied. Catalytic performance of praseodymium-modified beta zeolite shows highest cumene conversion (86.4 wt%) and cymene selectivity (65.7 wt%) compared to other zeolites. The maximum cumene conversion and cymene selectivity were obtained at 523 K, toluene-to-cumene ratio of 9:1, and a space time of 9.29 kg h/kmol. Kinetic modeling of the reaction was done to estimate the reaction kinetic constants and adsorption constants. The activation energy of the transalkylation was found to be 61.44 kJ/mol.

Keywords Beta zeolite · Rare earth metals · Transalkylation · Cymene · Cumene · Toluene

Abbreviations

Ce	Cerium
CeB	Cerium-modified beta zeolite

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DIPT	Diisopropyltoluene
Hbeta	Beta zeolite
k ₁ , k ₂ , k ₃	Kinetic constant, kgmol/kg h
Kc	Adsorption constant for cumene, atm^{-1}
K _t	Adsorption constant for tolene, atm ⁻¹
La	Lanthanum
LaB	Lanthanum-modified beta zeolite
Р	Total pressure, atm
p_{A}	Partial pressure of aliphatics, atm
$p_{\rm ben}$	Partial pressure of benzene, atm
P _{cum}	Partial pressure of cumene, atm
p _{cymene}	Partial pressure of cymene, atm
p_{DIPT}	Partial pressure of DIPT, atm
Pr	Praseodymium
PrB	Praseodymium modified beta zeolite
p_{xyl}	Partial pressure of xylene, atm
Pt	Partial pressure of toluene, atm
$-r_{\rm cum}$	Experimental rate of cumene conversion
X_{A}	Moles of aliphatics produced, kgmol
$X_{\rm ben}$	Moles of benzene produced, kgmol
$X_{\rm cum}$	Moles of cumene reacted, kgmol
X _{cymene}	Moles of cymene produced, kgmol
X_{DIPT}	Moles of DIPT produced, kgmol
X_{expt}	Experimental fractional conversion
$X_{ m xyl}$	Moles of xylene produced, kgmol
$X_{\rm pred}$	Predicted fractional conversion
X_{t}	Moles of toluene reacted, kgmol
τ	Space-time, kg h/kgmol

Introduction

Aromatics have numerous applications in the chemical and petrochemical industries (Odedairo and Al-Khattaf 2011). Transalkylation which includes transfer of alkyl group from

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one molecule to another is one of the prominent catalytic processes for the conversion of aromatics, especially for the production of industrially important products like xylenes, ethylbenzene, cumene, and cymene (Brown and Nelson 1953). The main significance of this class of reaction lies in the fact that low-valued polyalkylated benzenes could be converted to monoalkylated substitutes having higher commercial value. The products of transalkylation reactions have commercial importance as they are derived from low-valued by-products like diethyl or diisopropyl benzenes, toluene, and benzene. Among benzene, toluene, and xylenes (BTX), the price of toluene is always the lowest. Therefore, an attempt to transalkylate low-valued toluene to industrially important product is of great commercial value.

Early research work in this area was carried out to convert toluene to important industrial aromatics (Brown and Nelson 1953). Transalkylation of toluene with trimethylbenzene was carried out for the production of xylene in which transfer of methyl group from TMB to toluene initiates the reaction (Chao and Leu 1989; Das et al. 1994; Dumitriu et al. 1996, 2002). Similarly, transfer of other alkyl groups like ethyl or isopropyl group can lead to the formation of ethylbenzene, 4-alkyl- or 4,4'-dialkyl biphenyls or naphthalenes, and cumene in transalkylation reaction (Maity et al. 2006; Kondamudi and Upadhyayula 2008). Recent studies have shown various approaches of transalkylation that it can be combined with other processes like dealkylation to maximise the product yield (Abichandani et al. 2015; Abudawoud 2015). Lowpressure transalkylation can be operated which give better results than typical transalkylation process (Rashid et al. 2014). Recent transalkylation processes are not only limited to C-C bonds and simple aromatics, but temperature-induced transalkylation of C-N bonds has been reported by Obadia et al. (2015) and transalkylation of complicated aromatics such as polycyclohexylbenzenes and fullerenes can also be carried out (Nikita et al. 2014; Wang et al. 2010).

Toluene is usually produced in the processes for gasoline production by catalytic reforming. Low-valued toluene can be used for industrially valued product cymene. Cymenes, specially para and meta isomers, are important products, because it acts as a starting materials for the production of a range of intermediates and end products, such as cresols, fragrances, pharmaceuticals, pesticides, herbicides, polymers, and solvents (Reddy et al. 1995; Fraenkel and Levy 1989). It is also used as heat transfer agents. Alkylation of toluene with propylene or isopropyl alcohol is a well-known industrial route for cymene production. This method yields a mixture of cymene isomers (Rumyantseva et al. 2011). However, the preferred isomer distribution requires low ortho-cymene content as this isomer is difficult to oxidise (Odedairo and Al-Khattaf 2011). The main disadvantage of this method of cymene production is that this method uses hazardous Friedel-Crafts conditions over acid catalysts, such as H₂SO₄,

AlCl₃, TiCl₄, supported alumina, supported H₃PO₄, supported titania (Cullilane and Leyshan 1954; Flockhart et al. 1981), etc. The liquid catalysts are replaced by these solid acid catalysts as the solid catalysts are easy to regenerate; easy to separate from product and also have higher activity, selectivity and noncorrosiveness (Ghiaci et al. 2007; Bandyopadhyay et al. 1996, 1998).

Cymene can be produced by transalkylation of toluene with cumene. Very few attempts have been made in literature to explore the application of different types of medium- and largepore zeolites in transalkylation of toluene with cumene for the production of cymenes (Mavrodinova et al. 2003a, b). Banyopadhyay et al. (1996) investigated the transalkylation of cumene with toluene over H-beta, H-Y, and H-ZSM-12. Among the three catalysts, beta zeolite was found to be most active and selective catalyst. Banyopadhyay et al. (1998) compared two different routes of cymene production, namely transalkylation of toluene with cumene and other transalkylation of toluene with diisopropylbenzene. They concluded that large-pore zeolites favour bimolecular pathway. Mavrodinova et al. (2003a, b) carried out transalkylation of toluene with cumene over dealuminated Y zeolite and reported that replacement of framework Al by silicon resulted in the increase in strength and stability of acid sites. Odedairo and Al-Khattaf (2011) also performed toluene-cumene transalkylation over USY and dual zeolite comprising mordenite and ZSM-5. Dual zeolite-based catalyst gave higher toluene conversion and cymene selectivity. A bimolecular mechanism for n-propyltoluene formation has been proposed by Cejka et al. (1994). The desorption/transport of bulky propyltoluenes from the zeolite channel systems was found to be the reaction rate controlling step and zeolite type was found to have a crucial role in n-propyltoluene formation. Cejka and Wichterlova (2002) and Khattaf et al. (2014) reviewed major reactions of mono-, di-, and tri-alkylbenzenes, such as disproportionation, alkylation, transalkylation, isomerisation, etc., over different zeolites. The authors concluded that structural type, morphology, acid sites, accessibility of acid sites, and shape selectivity play crucial role in transformations of aromatics.

The most important technique used to modify zeolite is ion exchange. Metals ions belonging to groups like alkali and alkaline earth, transition, and rare earth elements are often regarded as promoters for zeolite catalysts (Rahimi and Karimzadeh 2011). Modification by metal ions is reported to enhance the activity, selectivity, and stability of zeolites. Metal-modified zeolites are applied for a number of chemical reactions (Arvela et al. 2013; Srilatha et al. 2012). Metalmodified zeolites are also extensively used for transalkylation reactions (Serra et al. 2005; Kauffman 1968).

However, it was observed from the literature that largepore zeolites like beta, mordenite, and rare earth metalmodified X and Y are effective catalysts for various transalkylation reactions (Cricsery 1971; Wang et al. 1990). Metal ion-modified zeolites are known to possess higher activity and stability due to increased acidity of modified catalyst (Marakatti and Halgeri 2015; Peter et al. 2012; Pieter et al. 2010; Xiaomin et al. 2014). There is no information in the literature on the use of beta zeolitemodified with rare earth metal ions for these reactions. This study focuses on the catalytic performance of beta zeolite modified with various rare earth metal ions. Kinetic modeling is also done for the estimation of kinetic and thermodynamic constants involved in the reaction.

Experimental

Materials and reagents

Commercially available beta zeolite, in the form of extrudates (1.5 mm), was obtained from Sud Chemie, Vadodara, India. All chemicals used in the study were of high purity (>99%). Toluene and cumene were procured from Merck, India and Sigma-Aldrich, respectively. Ceric ammonium nitrate, praseodymium ammonium nitrate, and lanthanum ammonium nitrate were supplied by CDH Chemicals India. Nitrogen gas of grade–I (99.999% purity) was procured from Sigma gases and Services, India.

Equipment used for characterization

Energy Dispersive Spectroscopy (EDS) of the samples was done on Quanta 200FEG to confirm the metal exchange. ICP of the samples was done to find the elemental composition of the samples. To remove any organic content, 20 mg of zeolite sample was added to 25% of hydrogen peroxide solution, followed by the evaporation of liquid. To this sample, 0.5 ml of HNO₃ and 1.5 ml of HCl were added and were kept on the hot plate for 12 h at 353-363 K temperature. The sample was then cooled and 2 ml HCl was added to form a clear solution. This solution was evaporated completely. To this sample, 2-3 drops of HNO₃ were added and the volume was made up to 100 ml. The solution was then filtered and taken for sample analysis. Crystallinity of the powder zeolite samples was determined using X-ray diffraction patterns recorded on Bruker Angle X-ray Scattering, Diffractometer D8, Germany equipped with Ni-filtered Cu K-a radiation source. The XRD of the samples was done at a scanning speed of $2^{\circ}(2\theta)$ per minute with 2θ value in the range of 5°-60°. Sample preparation for the X-ray analysis involved gentle grinding of the solid into a fine powder. Approximately, 0.1-0.2 g of the sample was taken into the sample holder with slight compression to make it flat and tight. Brunauer-Emmett-Teller (BET) surface area analysis was carried out for the virgin and the modified zeolites using CHEM-BET 3000 instrument, Quantachrome.

The acidity of the catalyst samples was determined using ammonia temperature programed desorption (CHEM-BET 3000 instrument, Quantachrome). For acidity determination, catalyst sample (0.1 g) was degassed at 723 K for 1 h under inert atmosphere using nitrogen followed by cooling to 273 K. Nitrogen–ammonia gas mixture (1 mol% ammonia) was then passed through the sample for 1 h. The catalyst sample was heated to 372 K until the equilibrium was attained; thereafter, the temperature of the sample was raised up to 1173 K at a heating rate of 10 K/min and then the desorbed ammonia was detected by a Thermal Conductivity Detector analyzer. Studies of FTIR were done using Agilant Cary-660 spectrophotometer.

Catalyst preparation

Before ion exchange, the H-beta zeolite extrudates were calcined for 3 h at 623 K to remove any impurity or gas present. Ion exchange was carried out by refluxing the calcined zeolite extrudates with lanthanum/ceric/praseody-mium nitrate solution of required concentration at 363 K for 24 h. The modified zeolite was filtered from the solution and washed with deionised water to remove excess ions. This ion exchanged zeolite was then dried at 393 K for 14 h and further calcined for removal of excess gases for 4 h at 723 K.

Determination of metal in exchanged catalyst

The amount of rare earth metal ions was determined by the method given in the literature (Krishnan et al. 2002). The freshly calcined-modified zeolite was taken in a flask and digested for 1 h in concentrated HCl. The digested catalyst was washed with distilled water and filtered. The filtrate was transferred to a beaker and its volume was made up to about 250 ml by adding distilled water. 50 ml of saturated oxalic acid solution was mixed to this solution, which produced a white precipitate of cerium oxalate. The precipitate was then filtered using a Whattman no. 40 ashless filter paper and washed with distilled water. The filter paper was ignited in a previously weighed silica crucible at 1173 ± 10 K to a constant weight. On heating, rare earth metal oxalate was converted to rare earth metal oxide. From the weight of metal oxide, the percentage of metal present in the zeolite was then calculated.

Transalkylation

Kinetic runs were carried out in a fixed-bed, continuous downflow reactor (SS 316) in vapour phase at 1 atm. Before conducting the experiments, catalyst was activated using nitrogen at a flow of 0.565 L/h (at 100 K higher than the reaction temperature) for 3 h. Reactant feed was introduced into the catalytic reaction system with the help of a pump. Nitrogen to feed flow ratio was kept constant during all experimental runs. The liquid product samples were collected by condensing the product vapors in a condenser. These samples were analyzed in a gas chromatograph equipped with FID detector. The deviations in the results are in the range of $\pm 2\%$.

The cumene conversion and cymene selectivity were calculated as:

Cumene conversion =
$$\frac{\text{Cumene in feed} - \text{Cumene in exit}}{\text{Cumene in feed}}$$

× 100

Cymene selectivity

 $=\frac{\text{Cymene in product mixture}}{\text{Aromatics in products excluding toluene and cumene}} \times 100.$

Toluene-cumene transalkylation can be represented as following reaction scheme:



Results and discussion

Characterization of modified catalyst

EDS of all zeolite samples (parent and modified) confirmed that metal exchanged has been successfully carried out. The metal ion concentration (wt%) in beta zeolite was determined by ICP. The amount of metal ions present (wt%) in the modified zeolite is given in Table 1.

XRD of all four samples (Fig. 1) showed that the framework structure of the zeolite was intact after metal ion exchange. The intensity of the peaks decreased in modified zeolites, which shows that crystallinity of beta zeolite decreased on metal exchange. The diffractogram of parent zeolite exhibited high-intensity reflections at 2θ value of 7.8° (101) and $21^{\circ}-22^{\circ}$ (302) which are typical characteristic peak of beta zeolite (Zhang et al. 2014). The crystallinity of the modified samples was obtained by comparing the intensity of these peaks with parent zeolites. The degree of crystallinity of modified samples was found to be in the order of La > Ce > Pr based on their electropositivity.

Degree of crystallinity % = peak intensity of zeolite sample at peak 2θ value $21^{\circ}-22^{\circ}$ /peak intensity of reference sample at peak 2θ value $21^{\circ}-22^{\circ}$.

Temperature-programmed desorption of ammonia for the zeolite samples is shown in Fig. 2. The profiles show that PrB zeolite is most acidic of all four zeolites. Acidity decreases in the order PrB > CeB > LaB > HB. The beta zeolites mainly contain two types of acid sites of different strengths. For a sample, TPD peak obtained at low-temperature peak is due to desorption from the weak acid sites, whereas the peak at high temperature is due to desorption from strong acid sites. Figure 2 shows that in the case of HB zeolite, weak acid sites are present mainly; however, a very small peak at higher temperature is also present. For modified zeolite, the low and high temperature peaks shows the presence of both type of acidic sites. As the acidity of the zeolite increased with exchange of different metal ions desorption peaks slightly shifted towards the higher temperature. The number of acid sites also increased as the peak area increased with metal exchange. Thus, metal ion exchange leads to increase in both quantity and strength of the acid sites in zeolite. This has also been observed by Wang and Zou (2003) in their study on Fries rearrangement. The acidity of various zeolites is reported in Table 1. It was found that the acidity of PrB was highest among all the samples. This may be due to combined effect of charge and size of Praseodymium. This trend of acidity may be explained on the basis of combined effect

Catalyst	Metal (wt%)	Crystallinity (%)	Bronsted acidity (mmol/gm)	Lewis acidity (mmol/gm)	Surface area (m ² /g)
HB	NIL	100	0.53	0.26	633
LaB	7.95	93	0.63	0.58	526
CeB	7.93	91	0.76	0.87	545
PrB	7.89	89	0.90	0.98	554

Table 1 Physiochemical properties of various catalysts



Fig. 1 XRD of zeolite samples

of charge and size. Higher charge and small size increase charge-to-size ratio and hence acidity also increases.

Pyridine being a strong base is favoured as a probe molecule in pyr-FTIR for quantification of both bronsted and lewis acid sites. Pyridine molecules interact with bronsted acid sites to form pyridinium ions which give IR bands around 1540 and 1640 per cm, whereas pyridine coordinatively bonded to lewis acid sites gives bands around 1450 and 1622 per cm. A band corresponding to combination of bronsted and lewis acid sites is observed at 1490 per cm (Fig. 3). It was observed that bronsted/lewis acidic sites ratio decreased on modification of the zeolites with metal ions. This shows that lewis acidity increased with ion exchange of zeolite. As activity of the zeolite was found to increase with metal exchange; therefore, it can be concluded that lewis acidity controls the activity and hence transalkylation.

The surface area of the zeolites was obtained from nitrogen adsorption using BET technique (Fig. 4). Incorporation of metal ions in zeolite pores reduces surface area in exchanged zeolites. The surface area values (Table 1) show that the surface area of modified zeolites depends on the diameter of metal ion; larger ion resulted in decrease in surface area.



Fig. 2 Ammonia-TPD profile of various beta zeolites

Effect of zeolite activity on product distribution

For 3 h time on stream, it was observed (Fig. 5) that all the metal exchanged zeolites were active in catalysing the transalkylation of cumene to cymene. Difference in the activity of the zeolites may be attributed zeolite structure, acidity, and nature of metal ion. It was observed that higher acidity resulted in higher activity. Praseodymium-modified beta zeolite (PrB) was found to be the most active catalyst which gave 86.4% conversion of reactant (cumene). The highest activity of praseodymium-modified beta zeolite may be due to highest charge-to-size ratio which leads to formation of highly concentrated acidic sites and thus increases the acidity and activity of the zeolite. The further kinetics studies were performed using PrB as catalyst for transalkylation.

Effect of praseodymium loading in the zeolite

To study the effect of praseodymium loading in beta zeolite, the zeolite was loaded with different amounts of praseodymium nitrate solution (2, 6, 10, and 14 wt%). The modified zeolites were found to contain 1.5, 4.7, 7.9, and 11.2 wt% amount of praseodymium (obtained from EDS). Figure 6 shows that cumene conversion increases with increase in praseodymium loading on the catalyst.



Fig. 3 Pyridine FTIR of various zeolites



Fig. 4 BET profile of various beta zeolites

However, the zeolite with praseodymium loading of 14 wt% showed considerable decline in cumene conversion with time on stream. This may be due to the presence of the strong acid sites which initiated side reactions leading to coke formation causing fast deactivation of the catalyst. Similar observation has been reported on deactivation study of zeolites in thermocatalytic deoxygenation of bi-oil (Alaba et al. 2016). Therefore, further study was done using 10 wt% praseodymium loaded zeolite (PrB₁₀).

Effect of catalyst loading in the reactor

Catalyst loading was varied from 1.44 to 8.63% (w/w) of the reactants, as shown in Fig. 7. The conversion of reactant (cumene) showed sharp increase with increase in catalyst loading from 1.44% (w/w) to 5.76% (w/w) due to the presence of large number of active sites available for the reactants. However, above catalyst loading of 5.76% (w/w) increase in cumene conversion was not significant



Fig. 5 Effect of rare earth metal ion modification on cumene conversion. Reaction conditions: pressure 1 atm, temperature— 523 K, toluene/cumene mole ratio of—9:1, space time—9.29 kg h/ kmol, 2 g catalyst, N₂ feed flow rate—0.20

(86.4-87.3%) at 523 K, toluene/cumene ratio 9, and 9.2 kg h/kmol space time. Therefore, 5.76% (w/w) loading of catalyst in the reactor was found to be optimum.

Effect of reaction temperature

Reaction temperature influences the rate of reaction and yield of products very strongly as intrinsic rate constants are function of reaction temperature. To study the effect of reaction temperature on reactant conversion and product selectivity, reaction was carried out in the temperature range of 448-573 K. The product distribution at different temperature is given in Table 2, which shows that the temperature has a significant effect on product distribution. The cumene conversion increases with increase in temperature. However, the increase is not appreciable after 523 K showing an increase of only 2.2% (86.4-88.6%) up to 573 K. In addition, cymene yield (16.2 wt%) and cymene selectivity (65.7 wt%) were found to be maximum at 523 K. At higher temperature (>523 K), side products like benzene, xylene, and DIPT yield increase due to dealkylation and disproportionate reactions. Disproportionation of cumene and cymene was negligible as DIPB and DIPT were formed in negligible amount. Among the side products, yield of benzene was maximum.

Effect of reactant ratio

The transalkylation reaction was carried out by varying toluene-to-cumene mole ratios from 1 to 15 at a reaction temperature of 523 K and space time of 9.29 kg h/kmol. As shown in Fig. 8, the cumene conversion was maximum (86.4 wt%) at a toluene-to-cumene mole ratio of 9:1. Above



Fig. 6 Effect of praseodymium loading on toluene conversion. Reaction conditions: Pressure 1 atm, Temperature—523 K, Toluene/cumene mole ratio of—9:1, space time—9.29 kg h/kmol, 2 g catalyst, N_2 feed flow rate—0.20

this mole ratio, the active sites are crowded by the excess reactant (toluene) which reduces the availability of active sites to limiting reactant (cumene) and hence lead to decrease in cumene conversion. Cymene selectivity was found to increase with increase in toluene-to-cumene mole ratio. Benzene yield decreases with increasing toluene-to-cumene mole ratio which shows that benzene is formed by dissociation of cumene rather than toluene disproportionation.

Effect of space time

The effect of space time was studied by keeping the weight of catalyst constant and varying the flow rates of the feed. The space–time range chosen for study was 3.20–9.29 kg h/kmol



Fig. 7 Effect of catalyst loading on cumene conversion in 3 h time on stream. Reaction conditions: pressure 1 atm, temperature—523 K, toluene/cumene mole ratio of—9:1, space time—9.29 kg h/kmol, N_2 feed flow rate—0.20

at a temperature of 523 K and reactant ratio of 9:1. Cumene conversion was found to increase with increase in spacetime (Table 3). The higher space-time allows the reactant molecules to stay over the catalyst for enough time to react resulting in higher yield of products. With increase in space time, cymene yield and cymene selectivity were also found to increase. Disproportionation of toluene and cymene both increased with increase in space time which is evident from higher yield of side products.

Kinetics of transalkylation

Mass transfer considerations

In any kinetic regime, the effect of external and internal mass transfer resistance should be negligible. Experiments were carried out using different amounts of catalyst (2 and 4 g) at constant space–time to investigate external diffusional effects. Feed rate was varied during the runs so as to keep the space time constant. The results presented in Table 4 show that cumene conversion remains almost the same in both the cases which confirm complete absence of external diffusional resistance.

To study the intraparticle diffusional effects, experiments were carried out at constant space-time with different particle size (0.5–1.5 mm). Cumene conversion remained same over different size catalyst particles (Table 5). This showed that the catalyst used in the kinetic study was free from intraparticle diffusion resistance.

Langmuir-Hinshelwood-Hougen-Watson model

The experimental data were fitted in the LHHW model to evaluate various rate constants of different reactions. It is seen from the product distribution that cymene and benzene are formed in fair amount. As DIPB was produced in negligible amount, cumene disproportionation was neglected in preparing the model. The following rate expression using the L–H–H–W model with surface reaction as a rate controlling step and dual site (both reactants adsorbed on catalyst) mechanism was found to fit the kinetic data significantly better than the other models.

$$-r_{\rm cum} = dX_{\rm cum}/d\tau$$
$$= \left(k_1 K_t K_{\rm cum} p_t p_{\rm cum} + \left(\frac{k_2}{C_v}\right) K_{\rm cum} p_{\rm cum} + k_3 (K_{\rm cum}^2) (p_{\rm cum}^2)\right) (C_v^2)$$
(1)

where $Cv = 1 + K_C p_C K_{TMB} p_{TMB} + K_T p_T$. The partial pressures in the above equations were calculated using the fractional conversions and total pressure *P* as given by the following expressions. In the reaction system, the total

Table 2Product distributionsfrom the transalkylation oftoluene and cumene overdifferent temperatures

Product distribution (wt%)	Temperature (K)							
	448	473	500	523	548	573		
Aliphatics	0.10	0.12	0.12	0.13	0.11	0.10		
Benzene	2.98	4.93	5.84	7.12	7.89	8.03		
Toluene	82.7	79.18	76.93	73.60	73.39	73.81		
Xylene	0.09	0.10	0.17	0.21	0.32	0.54		
Cumene	7.22	4.54	3.12	1.74	1.61	1.46		
Cymene	6.21	10.32	12.92	16.21	15.43	14.83		
DIPT	0.70	0.81	0.90	0.99	1.25	1.23		
Cumene conv. (wt%)	43.6	64.5	75.6	86.4	87.4	88.6		
Cymene selectivity (wt%)	61.6	63.4	64.8	65.7	61.7	60.0		

Reaction conditions: pressure 1 atm, toluene/cumene mole ratio of—9:1, space-time—9.29 kg h/kmol, 2 g catalyst, N_2 feed flow rate—0.20

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Fig. 8 Effect of reactant ratio on product distribution. Reaction conditions: pressure 1 atm, temperature—523 K, 2 g catalyst, space-time—9.29 kg h/kmol, N_2 feed flow rate—0.20

number of moles of different components was found to be 12. The values of $p_{\rm T}$ and $p_{\rm cum}$ calculated at various space time are reported in Table 6.

 $p_{\rm T} = (9 - X_{\rm T})P/12 \tag{2}$

$$p_{\rm cum} = (1 - X_{\rm cum})P/12$$
 (3)

$$p_{\rm cymene} = (X_{\rm cymene})P/12 \tag{4}$$

$$p_{\rm ben} = (X_{\rm ben})P/12 \tag{5}$$

$$p_{\rm xyl} = (X_{\rm xyl})P/12 \tag{6}$$

$$p_{\text{DIPT}} = (X_{\text{DIPT}})P/12 \tag{7}$$

$$p_{\rm A} = (X_{\rm A})P/12.$$
 (8)

Parameters of the model were estimated by nonlinear regression. The experimental rates at various temperature and space time were calculated using formula and the values are reported in Table 7.

$$-r_{\rm cum} = \mathrm{d}X_{\rm cum}/\mathrm{d}\tau \tag{9}$$

The optimum value of the parameters was estimated by minimizing the objective function given by equation. The kinetic and adsorption constants were evaluated and are shown in Table 8.

Product distribution (wt%)	Space-time (kg h/kmol)								
	3.2	3.57	4.04	5.16	6.507	9.29			
Aliphatics	0.3	0.08	0.09	0.13	0.11	0.13			
Benzene	4.29	5.08	5.30	6.63	6.82	7.12			
Toluene	84.10	82.94	81.30	78.23	77.10	73.60			
Xylene	0.0	0.11	0.14	0.17	0.19	0.21			
Cumene	5.91	4.74	3.59	2.31	1.94	1.74			
Cymene	5.19	7.03	9.14	11.9	13.03	16.21			
DIPT	0.12	0.29	0.44	0.63	0.81	0.99			
Cumene conv. (wt%)	53.8	63.0	71.9	81.9	84.8	86.4			
Cymene selectivity (wt%)	51.9	52.8	60.5	61.1	62.2	65.7			

Reaction conditions: pressure 1 atm, temperature—523 K, 2 g catalyst, N_2 feed flow rate—0.20

Table 3 Product distributionfrom the transalkylation oftoluene and cumene at differentspace-time at 523 K

Table 6

Table 4 Effect of external diffusion

Space-time (kg h/kmol)	Conversion of cumene (%)					
	Catalyst weight = 0.002 kg	Catalyst weight = 0.004 kg				
4.04	62.8	63.5				
5.16	66.6	67.2				
6.20	70.4	71.2				

Reaction conditions: pressure 1 atm, reaction temperature—498 K, toluene/cumene mole ratio of—9:1, space time—9.29 kg h/kmol, PrB10 (1.5 mm) catalyst, N2 feed flow rate—0.20

Table 5 Effect of internal diffusion

Particle size dp (mm)	Conversion of cumene (%)	Conversion of cumene (%)						
	space-time(kg h/kmol) = 4.04	space-time(kg h/kmol) = 5.16	space-time(kg h/kmol) = 6.20					
0.50	63.6	62.7	71.4					
1.00	63.2	67.0	70.9					
1.50	62.8	67.0	70.4					

Reaction conditions: pressure 1 atm, reaction temperature—498 K, toluene/cumene mole ratio of—9:1, space-time—9.29 kg h/kmol, PrB₁₀ (1.5 mm) catalyst, N_2 feed flow rate—0.20

Table 6 Calculated p_{cum} and p_t at various space–time	Space-time (kg h/kmol)	$P_{\rm c} = (1$	$-X_{\rm c}){\rm P}/12$	(atm)		$p_{\rm t} = (9 - X_{\rm t})P/12 \ ({\rm atm})$			
-		523 K	498 K	473 K	448 K	523 K	498 K	473 K	448 K
	4.0	0.0233	0.0372	0.0417	0.059 8	0.7443	0.7464	0.7473	0.7486
	5.16	0.0150	0.0278	0.0381	0.0543	0.7413	0.7433	0.7446	0.7474
	6.20	0.0126	0.0246	0.0345	0.0506	0.7403	0.7417	0.7438	0.7464
	9.29	0.0113	0.0203	0.0295	0.0469	0.7370	0.7401	0.7423	0.7457

Table 7 Experimental rate at various temperatures and space-time

Space-time (kg h/kmol)	Experimental rate (kmol/kg h)				
	523 K	498 K	473 K	448 K	
4.04	0.1780	0.1554	0.1235	0.0656	
5.16	0.1588	0.1290	0.1050	0.0627	
6.20	0.1366	0.1134	0.0941	0.0631	
9.29	0.0930	0.0813	0.0694	0.0470	

$$f = \sum_{i=1}^{n} [(\text{Rate predicted})i - (\text{rate experimental})i]^2. \quad (10)$$

The standard error of estimate for the rate of disappearance of cumene was 6.90×10^{-4} which was calculated using the values of constants from Table 8. Figure 9 shows that experimental and predicted rates are quite comparable having an R^2 value of 0.97.

Activation energy and pre-exponential factor for transalkylation reaction were found to be 61.44 kJ/mol and 5.37×10^{9} , respectively, which was calculated from Arrhenius equation. The value of activation energy varying from 46 to 104.6 kJmol^{-1} in the temperature range 483-543 K for the transalkylation of *m*-diethylbenzene over beta zeolite is reported (Forni et al. 1995).

Deactivation kinetics

For a differential reactor, the deactivation constant may be assumed independent of reactant concentration. For a batch of solid (catalyst) and plug flow of fluid, the following equation may be used for determining the deactivation constant. A plot of $\ln[\ln(C_{A0}/C_A)]$ vs t at four temperatures is shown in Fig. 10; the slopes of the lines at different temperatures represent the deactivation constant k_d at the temperature under consideration. The value of deactivation constant was found to be lower than reaction constants. The values of $\ln k_d$ were plotted against 1/Temperature (Fig. 11) to find the apparent activation energy for deactivation of catalyst which was found to be 14.8 kJ/kmol

Kinetic and adsorption parameters	Temperatur	e		
	448 K	473 K	498 K	523 K
K_1 (kmol/kg h)	3.99	12.39	21.54	38.98
K_2 (kmol/kg h)	2.55	7.54	12.60	29.99
K_3 (kmol/kg h)	2.30	3.79	7.09	11.76
$K_{\rm c} (\rm atm^{-1})$	0.940	0.75	0.65	0.564
$K_{\rm t} ({\rm atm}^{-1})$	1.805	1.604	1.40	1.205



Fig. 9 Experimental vs predicted values of reaction rate



Fig. 10 Plots of $\ln[\ln(C_{AO}/C_A)]$ vs time at different temperatures

which is much lower than that for the main reaction. In case of alkylation and transalkylation reactions, the coke formed is olefinic in nature and hence is formed faster, so catalyst is more susceptible to pore blockage at low temperatures (Sridevi et al. 2001):

$$\ln\left[\ln\left(\frac{C_{A0}}{C_A}\right)\right] = \ln(k\tau') - k_d t.$$
(11)



Fig. 11 Arrhenius plot for deactivation energy

Conclusion

Toluene transalkylation with cumene was carried out over rare earth metal-modified large-pore zeolites. Rare earth metal ion modification caused a significant change in the activity of the catalyst by strengthening acidic sites and increasing the number of acidic sites. Difference in the activity of these zeolites depends on the properties related to the zeolite structure, acidity, and nature of the metal ion. Zeolite modified with rare earth metal ion gave higher reactant conversion, product yield, and selectivity compared to unmodified zeolite. Praseodymium-modified beta zeolite was found to be the best among various catalyst chosen for study. PrB₁₀ showed higher activity at 523 K than all other metal-modified zeolites. At high reaction temperature of 573 K, dealkylation and disproportionation are favoured which lead to decrease in yield and selectivity of cymene. High toluene-to-cumene ratio favors maximum cumene conversion and cymene yield. Cumene conversion was found to increase with increase in space time.

Based on the product distribution, a reaction mechanism was proposed together with a rate expression for the disappearance of toluene using LHHW approach. The kinetic and the adsorption constants of the rate equation during their various transformation reactions were estimated by the best fit. The activation energy for the cymene synthesis reaction was determined to be around 61.44 kJ/mol over praseodymium-modified zeolite.

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