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Alkylation of toluene with isopropyl alcohol catalyzed by Ce-exchanged NaX zeolite

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Abstract

The industrially important cymene synthesis was carried out by toluene isopropylation over cerium-exchanged NaX zeolite. The modification of NaX zeolite by cerium exchange was found to enhance the catalytic activity of the zeolite to a considerable extent. The reactions were carried out in a fixed-bed flow reactor at atmospheric pressure with nitrogen as the carrier gas. The reaction conditions were optimized by varying temperature, reactants mole ratio and space-time. It was observed that in the isopropylation of toluene, the isopropyltoluene fraction contained both *para* and *meta* isomers. There was no *ortho*-cymene in the product stream. Alkylation studies at 433–513 K showed a decrease in *p*-cymene selectivity with increase in reaction temperature and increased formation of diisopropyl toluene at lower temperature. A systematic and detailed kinetic study was carried out for the alkylation reaction. From the product distribution pattern, a kinetic model for the reactions was proposed by following Langmuir–Hinshelwood approach. The kinetic and adsorption parameters of the rate equation were determined by non-linear regression analysis. The apparent activation energy for the main reaction was found to be 48.12 kJ/mol.

Keywords: Alkylation; Toluene; Cymene; Ce-exchanged zeolite; NaX zeolite; Kinetics

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1. Introduction

Alkylation of toluene with isopropyl alcohol to produce cymenes is an industrially important reaction. Cymenes, specially the *para* and the *meta* isomers, are important starting materials for the production of a range of intermediates and end products, such as cresols, fragrances, pharmaceuticals, herbicides, heat transfer media, etc. [1–3]. Cymenes can be produced by alkylation of toluene with either propylene or isopropyl alcohol. A variety of Friedel–Craft catalysts, such as $FeSO_4$-HCl, $AlCl_3$, BF_3 or H_2SO_4 have been used for toluene isopropylation. However, over these catalysts, the proportion of the undesired *ortho* isomer is up to 5% and multialkylation cannot be prevented.

Besides the homogeneous Friedel–Craft catalysts, the solid acid catalysts are also used to produce *p*-cymene via alkylation of toluene with isopropyl alcohol [4–12]. This helps eliminate the corrosion and waste disposal problems associated with conventional Friedel–Craft catalysts. In 1989, Fraenkel and Levy [5] studied toluene isopropylation with isopropyl alcohol on protonic forms of medium pore zeolite ZSM-5 and large pore zeolite Y and proposed a reaction mechanism. Parikh et al. [6,7] studied the same reaction over zeolites having varying pore systems, crystal size and silylation extent and proposed a more realistic mechanism on Al-ZSM-5. In 1994, Cejka et al. [8] investigated the factors controlling *iso*-/*n*- and *para* selectivity in the alkylation of toluene with isopropyl alcohol over molecular sieves of varying acidity (Al- and Fe-silicates) and structural type (Y, mordenite and MFI structure). The effect of zeolite structural type on *n*-propyl toluene formation during C_3-alkylation of toluene had also been reported [9]. Reddy et al. [10] studied toluene isopropylation and reported selective formation of cymenes over large pore zeolites. Witchterlova et al. [11] investigated the selective formation of *p*-cymene on Al and Fe silicates. Medina-Valtierra et al. [12] studied the *para* selectivity in the alkylation of toluene with isopropyl alcohol on MCM-41/γ-Al_2O_3 catalyst. There is, however, no information in the literature on the use of more versatile zeolite X for cymene synthesis. Moreover, replacement of Na ions of synthetic zeolites (e.g., X and Y) with polyvalent cations from rare earth metals (La, Ce, etc.) has been reported to give materials of superior catalytic activity [13–16]. It was, therefore, thought desirable to investigate the kinetics of

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Nomenclature

A	isopropyl alcohol
DIPT	diisopropyl toluene
F	total feed rate (kgmol/h)
IPA	isopropyl alcohol
k_1	kinetic constant (kgmol/kg atm^2 h)
mcy	*m*-cymene
P	total pressure (atm)
pcy	*p*-cymene
p_A	partial pressure of IPA (atm)
p_{mcy}	partial pressure of *m*-cymene (atm)
p_{pcy}	partial pressure of *p*-cymene (atm)
p_T	partial pressure of toluene (atm)
T	toluene
τ	space-time of isopropyl alcohol (kg h/kgmol)
X_A	fractional IPA conversion
X_{exp}	experimental fractional conversion of IPA
X_{mcy}	mole fractional of *m*-cymene
X_{pcy}	mole fractional of *p*-cymene
X_{pred}	predicted fractional conversion of IPA
W	mass of the catalyst (kg)
W	water

this commercially important reaction over zeolite NaX modified by exchanging sodium ions with cerium ions.

2. Experimental

2.1. Materials

The NaX zeolite used in the present study was obtained from S. D. Fine Chemicals Pvt. Ltd., India. It was in the form of 1.5 mm extrudate. Isopropyl alcohol (IPA) and toluene used in this study were of ‘Analytical Reagent’ grade. Isopropyl alcohol was obtained from Qualigens Fine Chemicals, Mumbai, India and toluene from S. D. Fine Chemicals Pvt. Ltd.

2.2. Catalyst preparation

The NaX zeolite was first dried to remove moisture and kept ready for cation exchange. The catalyst particles were first refluxed with 2% NH_4NO_3 solution 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 [17]. 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.

2.3. Determination of cerium in the exchanged catalysts

Accurately 2 g of freshly calcined catalyst containing cerium was taken in a conical flask and digested with concentrated HCl for about an hour. The digested material was then diluted with distilled water and filtered through a filter paper. The filtrate containing the cerium in solution was transferred to a 500 mL beaker, and its volume was raised to about 250 mL by adding distilled water. To this solution, 50 mL of saturated oxalic acid solution was added, which gave rise to a white precipitate of cerium oxalate. The precipitate was filtered through a Whatman no. 40 ashless filter paper and was thoroughly washed with distilled water. The white precipitate along with the filter paper was then ignited over a previously weighed silica crucible at 1173 ± 10 K to a constant weight. On heating, cerium oxalate was converted to Ce_2O_3. The percentage of cerium was then calculated from the weight of Ce_2O_3 [18].

2.4. Temperature-programmed desorption (TPD) of ammonia

Ammonia TPD of the modified catalysts was performed in a CHEM-BET 3000 instrument (QuantaChrome, USA). In a typical experiment, 0.1 g of the powdered catalyst sample was taken inside a quartz “U” tube and degassed at 723 K for 1 h with helium gas flow followed by cooling to low temperature (∼303 K). The gas flow was then changed to 1 mol% ammonia in nitrogen for 1 h. After this, the helium gas flow was resumed once again for 30 min at the same temperature to remove loosely adsorbed ammonia molecules from the catalyst surface. The catalyst sample was then heated to 373 K under helium flow 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. The desorbed ammonia was detected by a TCD analyzer.

2.5. Experimental procedure and product analysis

The catalytic experiments were carried out in a fixed-bed, continuous down-flow cylindrical stainless steel (SS 316) tubular reactor (0.025 m i.d. 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 thermowell extending from the top of the reactor to the centre of the bed. The catalyst was activated ‘in situ’ for 6 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 alongwith nitrogen entered the reactor from the top. The product vapors, along with unreacted reactants, were condensed in the condenser and the liquid samples collected were analyzed in a gas chromatograph unit fitted with a 4.2 m × 3.2 mm SS column containing Benton 34 and 7% dinonyl phthalate stationary phase on Celite-545 solid support using a flame ionization detector (FID). The material balance was checked and it was >97%.

The term ‘conversion’ of IPA used in the kinetic studies is defined as:

$$\text{IPA conversion (\%)} = \frac{\text{moles of IPA consumed per unit time}}{\text{moles of IPA fed per unit time}} \times 100$$

The terms toluene conversion, cymene selectivity, *p*-cymene selectivity are defined as follows:

$$\text{toluene conversion (\%)} = \frac{\text{toluene in feed-toluene in product}}{\text{toluene in feed}} \times 100$$

$$\text{cymene selectivity (wt\%)} = \frac{\text{cymenes in product}}{\text{total aromatics (excluding toluene) in product}} \times 100$$

$$p\text{-cymene selectivity (wt\%)} = \frac{p\text{-cymene in product}}{\text{total aromatics (excluding toluene) in product}} \times 100$$

3. Results and discussion

3.1. Effect of cerium loading on toluene conversion

NaX zeolite was treated to exchange its sodium ions with cerium ions. This exchange was carried out with cerium nitrate solutions of different concentrations. The cerium content of the exchanged catalyst was estimated by a method described in Section 2. Table 1 presents the various Ce-exchanged catalysts with their cerium contents. Fig. 1 shows the plot of cerium concentrations in the catalysts versus toluene conversion at a toluene to isopropyl alcohol mole ratio of 6:1 and at a temperature of 493 K. As can be seen from the figure, the toluene conversion increases with increase in cerium content in the NaX zeolite and this may be due to stronger acid sites generated by the exchange.

Temperature-programmed desorption of ammonia was studied with NaX as well as Ce-exchanged NaX zeolites and Fig. 2 shows the TPD profiles of NaX, CeX_5 and CeX_{10} catalysts. The desorption of ammonia corresponding to different peaks is indicative of energy levels at which ammonia is bound to acid sites. The profiles indicate that the catalysts contain mainly two types of acid sites of different strengths. The strengths of the acid sites increase with Ce-exchange as the desorption peaks shift gradually towards the higher temperatures with increasing cerium content of the catalysts. 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. As CeX_{10} catalyst gave highest conversion compared to others, it was used for further study of the alkylation reaction.

Table 1
Cerium contents of various modified NaX zeolites

Catalyst designation	Concentrations of cerium nitrate solutions used for exchange (%)	Cerium content (wt%)
CeX_2	2.0	1.74
CeX_5	5.0	4.56
CeX_7	7.0	6.70
CeX_{10}	10.0	8.86
CeX_{12}	12.0	10.43

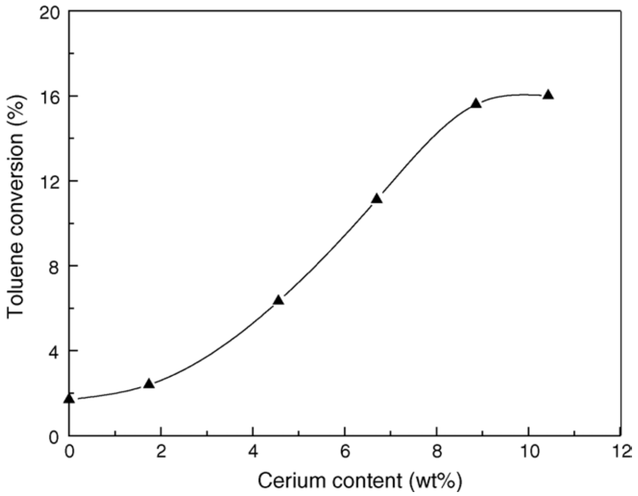

Fig. 1. Effect of cerium content on toluene conversion. Conditions: temperature 493 K; pressure 1 atm; toluene to IPA mole ratio 6:1; space-time 22.9 kg h/kgmol; nitrogen to feed ratio 0.5.

3.2. Time on stream behavior of CeX_{10}

The stability of Ce-modified NaX zeolite was tested for about 3.5 h time on stream at 493 K and atmospheric pressure. The

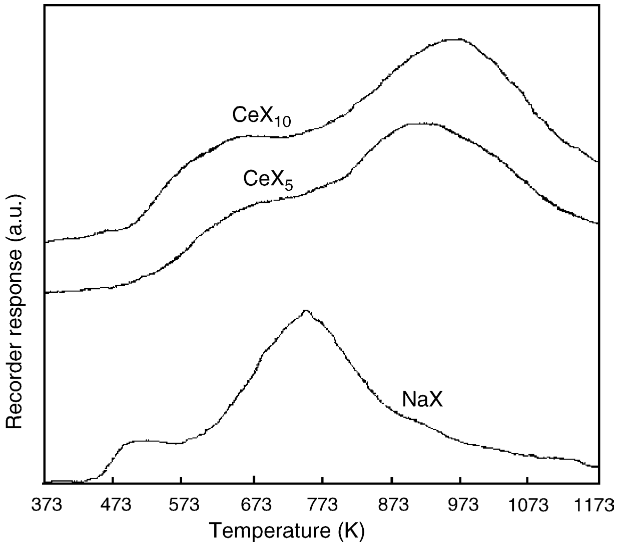

Fig. 2. Temperature programmed desorption profiles of ammonia for various catalysts.

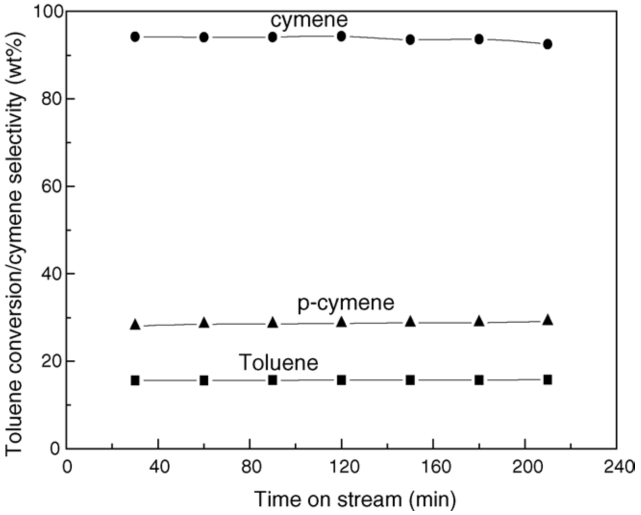

Fig. 3. Effects of time on stream on toluene conversion and cymene selectivity. Conditions: temperature 493 K; pressure 1 atm; toluene/IPA mole ratio 6:1; space-time 22.9 kg h/kgmol; catalyst CeX_{10}; nitrogen to feed ratio 0.5.

toluene conversion remained almost constant during this period as shown in Fig. 3. It is evident from this figure that the toluene conversion and cymene selectivity remain almost constant during 3 h time on stream over CeX_{10} zeolite catalyst. The catalyst is, therefore, very stable at the reaction conditions.

3.3. Effects of mole ratio of toluene to IPA on toluene conversion and cymene selectivity

The effects of feed mole ratio on toluene conversion and cymene selectivity are shown in Fig. 4. At low toluene to IPA mole ratio, the cymene selectivity is low, although toluene conversion is high, due to the formation of undesirable side product, diisopropyl toluene (DIPT) and aliphatics (Table 2). At higher toluene to IPA mole ratios, these side products are reduced showing an increase in the total cymene selectivity. At the same time, the isomerization of *para* to *meta* isomer seems to increase, and hence a decrease in *para* selectivity was observed with increasing toluene to isopropyl alcohol feed mole ratio. Toluene conversion drops at higher ratios, as may be expected, due to lower availability of the alkylating agent in the feed.

Table 2
Effect of toluene to IPA mole ratio on product distribution

Product (wt%)	Toluene to isopropyl alcohol mole ratio			
	0.5	2	4	6
Aliphatics	11.7	7.3	6.8	2.0
m-Cymene	49.5	54.8	56.1	62.2
p-Cymene	29.0	32.3	32.7	27.4
Total DIPT	9.8	5.6	4.4	3.4

Table 2 shows the products distribution obtained at various feed compositions. As can be seen from this table, higher amount of aliphatics and DIPT are formed with higher concentrations of alcohol in the feed.

3.4. Effects of temperature on toluene conversion and cymene selectivity

The effects of temperature on toluene conversion and cymenes selectivity are shown in Fig. 5 over CeX_{10} catalyst. The selectivity of cymenes was observed to increase with increase in temperature up to 493 K. Beyond this, a slight decrease in cymene selectivity was noticed.

At higher temperatures, dealkylation became pronounced, and hence selectivity of total cymenes was reduced. As the temperature was increased from 433 to 513 K, the *p*-cymene selectivity dropped from 42.62 to 26.34%, which is nearer to the equilibrium value of around 25%. Therefore, at higher temperatures, as a result of isomerization, the *p*-cymene is formed in almost equilibrium yield. A DIPT selectivity of 12% was observed at 433 K and it decreased with increase in temperature. However, no DIPT was detected in the product stream at temperatures higher than 525 K. An interesting observation

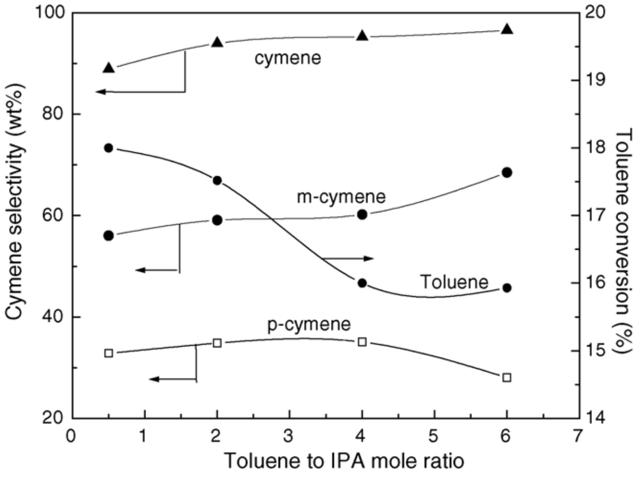

Fig. 4. Effects of toluene to IPA mole ratio on toluene conversion and product selectivity. Conditions: temperature 493 K; pressure 1 atm; space-time 22.9 kg h/kgmol; catalyst CeX_{10}; nitrogen to feed ratio 0.5.

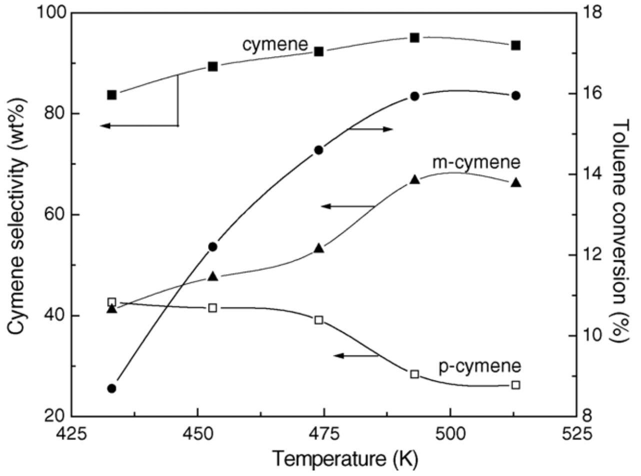

Fig. 5. Effects of temperature on toluene conversion and product selectivity. Conditions: pressure 1 atm; toluene to IPA mole ratio 6:1; space-time 22.9 kg h/kgmol; catalyst CeX_{10}; nitrogen to feed ratio 0.5.

Table 3
Para-cymene selectivity over various catalysts

Catalyst	Reaction conditions	*p*-Cymene selectivity (wt%)
HM [9]	Temperature 520 K; toluene to IPA mole ratio 9:1; space velocity 10 h^{-1}	23.4
HZSM-5 [9]	Temperature 520 K; toluene to IPA mole ratio 9:1; space velocity 10 h^{-1}	26.7
HY [9]	Temperature 520 K; toluene to IPA mole ratio 9:1; space velocity 10 h^{-1}	24.2
Hβ [10]	Temperature 453 K; toluene to IPA mole ratio 8:1; space velocity 4 h^{-1}	29.13
CeX_{10} (present work)	Temperature 513 K; toluene to IPA mole ratio 6:1; space velocity 3.8 h^{-1}	26.34

is that there is no *ortho* cymene detected in the product. The reason for this absence could be channel dimension of CeX_{10}, which prevents bigger *o*-cymene molecule to come out of the pores. Similar observation was made by Cejka and Wichterlova [19] and they concluded that zeolite channel geometry plays a decisive role in the product formation. The *p*-cymene selectivity obtained by other researchers with various zeolites having different channel geometry is presented in Table 3.

3.5. *Effect of space-time*

The effect of space-time on product distribution is shown in Fig. 6. The selectivity of cymenes was observed to increase with increase in space-time due to higher residence time in the reactor. Consequently, the yield of DIPT was found to decrease. As can be seen from Fig. 6, the *p*-cymene selectivity is relatively higher at lower space-times, probably because of suppression of the isomerization reaction of *p*-cymene to the *meta* isomer due to the lower residence time in the reactor.

3.6. *Mass transfer considerations*

For any kinetic study, it is important that the mass transfer resistances be negligible during the reaction. To estimate the external diffusional effects, experiments were carried out at constant space-time and catalyst size, but with varying feed rates.

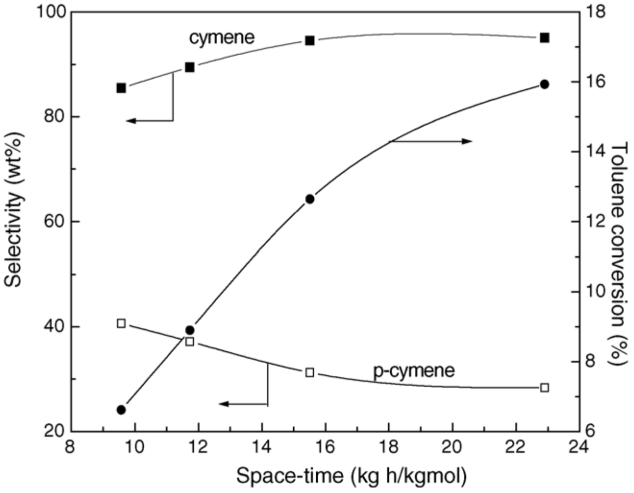

Fig. 6. Effects of space-time on toluene conversion and product selectivity. Conditions: temperature 493 K; pressure 1 atm; toluene to IPA mole ratio 6:1; catalyst CeX_{10}; nitrogen to feed ratio 0.5.

Table 4
Effect of external diffusional resistances on conversion of IPA

Space-time (kg h/kgmol)	Conversion of IPA (%) at	
	b	*c*
5.78	13.36	13.4
7.89	19.47	19.5
11.24	24.42	24.2

Conditions: temperature 402 K, toluene to IPA mole ratio 3:1; *b*: 0.03 kg CeX_{10} catalyst; *c*: 0.05 kg CeX_{10} catalyst; nitrogen to feed ratio 0.5.

The results shown in Table 4 indicate that the conversion of IPA for both the series at constant W/F are independent of feed rate. Therefore, the external mass transfer resistance is negligible. The minimum flowrate of feed employed was $3.33 \times 10^{-5}\ m^3/h$ corresponding to W/F ratio 5.78 kg h/kgmol. Experiments were also conducted to test the intraparticle diffusional limitations by varying the catalyst particle size while keeping space-time constant. The experimental data obtained are presented in Table 5. The results showed that there was no change in conversion of isopropyl alcohol with catalyst size indicating negligible intraparticle mass transfer resistance in the particle size range studied. The particle sizes employed in the kinetic study were within the intraparticle diffusion free range. In zeolite-catalyzed reactions, two types of diffusion processes are involved: (i) micropore diffusion inside the zeolite crystal and (ii) macropore diffusion between the zeolite crystals within the catalyst pellets. The above experiments for mass transfer resistances confirms only the absence of diffusion in the macropores. The resistance due to micropore could not be evaluated, as it requires a modification of the synthesis conditions of the zeolite that affect the micropore size of the crystals, which would subsequently affect the diffusional characteristics. Hence, the kinetic parameters presented here include these diffusional effects, if any.

Table 5
Effect of intraparticle diffusion on conversion of IPA

Particle size (mm)	IPA conversion (%) with space-time (kg h/kgmol) of		
	5.78	7.89	11.24
0.5	13.4	19.6	24.1
1.0	13.4	19.5	24.2
1.5	13.3	19.5	24.4

Conditions: temperature 402 K; toluene to IPA mole ratio 3:1; nitrogen to feed ratio 0.5.

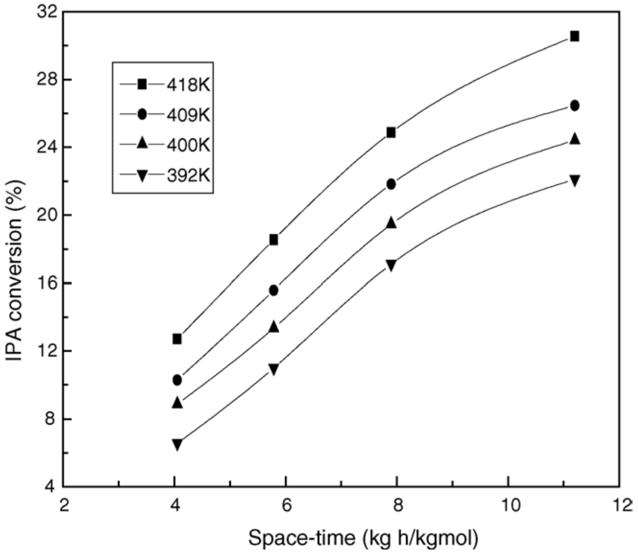

Fig. 7. Effect of space-time on IPA conversion. Conditions: pressure 1 atm; toluene to IPA mole ratio 3:1; catalyst CeX_{10}; nitrogen to feed ratio 0.5.

3.7. Kinetic studies

Kinetic runs were carried out under reaction conditions free of interparticle diffusional limitations. Toluene reacts with isopropyl alcohol to form *p*-cymene, which undergoes further isomerization to form *m*-cymene and *p*-cymene again reacts with isopropyl alcohol to form diisopropyl toluene. The kinetic studies were conducted at temperatures of 392, 400, 409 and 418 K, respectively. The conversions of IPA obtained at these temperatures are shown in Fig. 7 with space-time as abscissa. In the kinetic regime, the plausible reactions are:

$$\text{toluene}+\text{IPA}\xrightarrow{k_1} p\text{-cymene} + H_2O \tag{1}$$

$$p\text{-cymene} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} m\text{-cymene} \tag{2}$$

With the help of the reaction scheme, various reaction rate models (adsorption, desorption and surface reaction controlling) were formulated following Langmuir–Hinshelwood approach. The models were tested with the help of the experimental data. All models, except the surface reaction controlling one, gave unrealistic values of various constants with improper trends. Hence, they were not considered. The following surface reaction-controlling model was found to fit the experimental data better with proper trend of various constants.On the basis of dual-site mechanism, the following rate equation was obtained for the disappearance of IPA:

$$-r_A = \frac{dX_A}{d\tau} = \frac{k_1 K_T K_A \ p_T \ p_A}{Z^2} \tag{3}$$

where $Z = 1 + K_T p_T + K_A p_A + K_{pcy} p_{pcy} + K_{mcy} p_{mcy}$.

The adsorption of water and carrier gas was neglected in the above model. The partial pressures of various species are related to fractional conversions and total pressure (P) by the following expressions at an isopropyl alcohol conversion of X_A. Initially, 1 mole of IPA as the basis, the total moles present at any time sum up to 6.0. Hence,

$$p_A = \frac{(1 - X_A)P}{6.0} \tag{4}$$

$$p_T = \frac{(3 - X_A)P}{6.0} \tag{5}$$

$$p_{pcy} = \frac{X_{pcy} P}{6.0} \tag{6}$$

$$p_{mcy} = \frac{X_{mcy} P}{6.0} \tag{7}$$

$$p_W = \frac{X_A P}{6.0} \tag{8}$$

$$p_N = \frac{2.0 P}{6.0} \tag{9}$$

A non-linear regression algorithm was used for parameter estimation [20]. The optimum values of the parameters were estimated by minimizing the objective function given by equation:

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

The experimental and the predicted isopropyl alcohol conversions at four different temperatures were plotted in Fig. 8. It shows that the proposed reaction rate expression predicts the rate values comparable with the experimental rates. The kinetic and adsorption constants evaluated by non-linear regression are presented in Table 6. It is evident from this table that with increase in temperature the kinetic constants increase, whereas the adsorption constants decrease, which is as expected. The kinetic constant evaluated and tabulated at various temperatures were used to determine the apparent activation energy by using Arrhenius relationship and it was found to be 48.12 kJ/mol. The observed activation energy is close to that reported by Parikh et al. [7] for toluene isopropylation over ZSM-5. Similar activation energy values are also reported for toluene methylation over HZSM-8 [21] and for toluene ethylation over HZSM-5 [22].

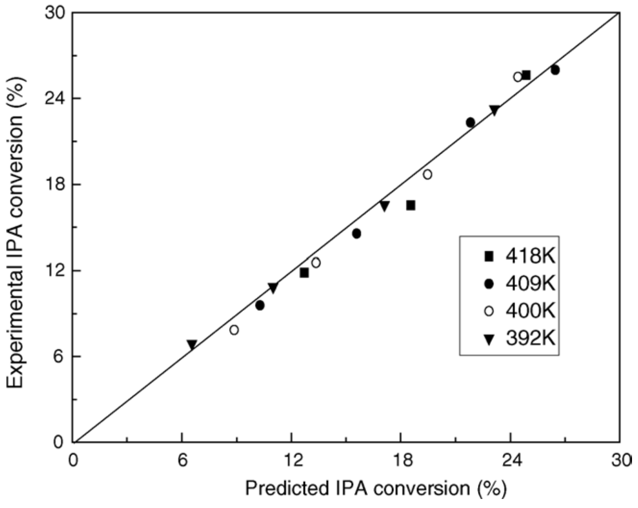

Fig. 8. Experimental vs. predicted IPA conversions.

Table 6
Kinetic and adsorption parameters of model equation

Parameters	Temperature (K)			
	392	400	409	418
k_1 (kgmol/kg h atm^2)	1.31	1.56	2.12	3.52
K_T (atm^{-1})	0.34	0.20	0.15	0.10
K_A (atm^{-1})	2.25	1.92	1.65	1.24
K_{pcy} (atm^{-1})	13.74	10.57	8.41	5.55
K_{mcy} (atm^{-1})	4.27	2.93	2.12	1.41

4. Conclusions

The isopropylation of toluene was carried out over Ce-exchanged NaX zeolite. Ce-exchanged zeolite containing 8.86 wt% cerium (CeX_{10}) was found to be the most stable and active catalyst among six different catalysts of different Ce contents. The activity and stability were found to be dependent on the acidic properties of zeolite. Higher cymene selectivity was observed at higher space-time and higher toluene to IPA mole ratios. The selectivity of cymenes went through a maximum in the temperature range of 433–513 K. The highest selectivity was observed at 493 K. A detailed kinetic study was performed. Based on the product distribution patterns, a kinetic model was proposed and the parameters of the model were estimated. From the estimated kinetic constant, the apparent activation energy for toluene isopropylation reaction was calculated to be 48.12 kJ/mol.

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