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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

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 station-