



Xylene isomerization side reactions over Beta zeolite: Disproportionation and transalkylation of C₈ aromatics and toluene

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ARTICLE INFO

Keywords:

Toluene
Ethylbenzene
Disproportionation
Transalkylation
Kinetics

ABSTRACT

An experimental and parametric behavior study of disproportionation and transalkylation between C₈ aromatics and toluene were carried out over mono-functional acid Beta zeolite with a SiO₂/Al₂O₃ ratio of 35 (BEA35). The experiments were performed in liquid phase under the following conditions: 453, 473, and 493 K and 2.1 MPa. Ethylbenzene disproportionation and ethylbenzene-toluene transalkylation were identified as the main side reactions; therefore, the kinetics of both reactions were estimated. Both reactions were verified to be second-order with no signs of competition for the adsorption sites under the studied conditions. Additionally, ethylbenzene disproportionation and ethylbenzene-toluene transalkylation, undergo through a deethylation-ethylation mechanism, the activation energies were 66 and 57 kJ/mol respectively. Furthermore, the existence of parallel reactions, as well as the feed concentration, showed no effect on the *p*-diethylbenzene selectivity. Selectivity towards the *para*-isomer was observed only at very low conversions. Finally, an analytical solution was developed for the system showing excellent agreement with the experimental data.

1. Introduction

The catalytic conversion of aromatic molecules and toluene via transalkylation or disproportionation is a very important process in the petrochemical industrial. Ethylbenzene (EB) disproportionation is one of the methods for the production of *p*-diethylbenzene (*p*-DEB) in the industry; compared with other processes, it needs lower installation costs, and has longer catalyst life [1]. *p*-DEB is the most desirable diethylbenzene (DEB) isomer, with wide range of applications in the chemical and petrochemical industry [2]; *p*-DEB is also used as desorbent in adsorptive separation processes such as Parex from UOP and Eluxyl from IFP. However, for a Simulated Moving Bed Reactor (SMBR), integrating the isomerization and adsorption of xylenes in a single unit, toluene (TOL) has been proposed instead *p*-DEB to act as desorbent, because of the isomerization of *p*-DEB [3–5]. Therefore, besides xylene isomerization, side reactions like disproportionation and transalkylation between C₈ aromatics and toluene may also exist within the SMBR unit.

Most of the literature studies on disproportionation and

transalkylation between C₈ aromatics and toluene focus on the influence of acid sites, different reaction mechanisms, and type of catalysts used. Both disproportionation and transalkylation reactions are recognized to have a strong link with Brønsted acid sites of the zeolite [6], which promote carbon-carbon bond scission [7]. In a study by Pan and co-workers on ZSM-5 [8], they revealed that both internal and external surfaces contain strong and weak acid sites. After the strong acid sites on the outside surface were poisoned by pyridine, the disproportionation results did not change. They demonstrated that the strong acid sites are the active sites for conversion of *p*-DEB and EB, but has little effect on *para*-isomer selectivity in disproportionation and isomerization. Also proved by Das et al. [9], the acid sites on the outside surface of ZSM-5 play a dominant role in the isomerization.

According to Santilli [10], two mechanisms are used to describe the transalkylation reaction. Firstly is the deethylation-ethylation mechanism, the alkyl group (R) is cleaved from the benzene ring to become R⁺, by the acid sites, and subsequently adds to another benzene ring. Another mechanism is via diphenylethane intermediate, a bulky intermediate is formed with two aromatic rings bridged by an R group.

Abbreviations: Bz, benzene; DEB, diethylbenzene; EB, ethylbenzene; ET, ethyl-toluene; EX, ethyl-xylene; MX, *m*-xylene; MR, membered rings; OX, *o*-xylene; PX, *p*-xylene; SMBR, Simulated Moving Bed Reactor; SAR, silica alumina ratio; TOL, toluene; TMB, trimethylbenzene

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<https://doi.org/10.1016/j.apcata.2018.06.011>

Received 12 April 2018; Received in revised form 5 June 2018; Accepted 6 June 2018
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Nomenclature		Greek letters	
C_i	Mass concentration of component i ($i = \text{Bz, TOL, EB, DEB, ET}$) (mol/L)	ε	Bed porosity
$E_{a,j}$	Activation energy of reaction j (kJ/mol)	ρ_p	Particle density (kg/m ³)
k_j	Kinetic constant of reaction j (m ⁶ /kg _{cat} s mol)	<i>Superscripts</i>	
$k_{0,j}$	Pre-exponential factor of reaction j (m ⁶ /kg _{cat} s mol)	i	Inlet
R_i	Rate of reaction i ($i = \text{Bz, TOL, EB, DEB, ET}$) (mol/kg _{cat} s)	o	Outlet
u	Fluid interstitial velocity (m/s)	<i>Subscripts</i>	
T	Temperature (K)	F	Feed
T_0	Centered temperature (K)		
z	Axial coordinate (m)		

Cleavage effect on the intermediate transfers the R group from one ring to the other. EB disproportionation reacts in a similar way; basically, the second requires larger space inside the zeolite.

Disproportionation and transalkylation over ZSM-5 occur through the deethylation-ethylation mechanism [11]. ZSM-5 is active for EB dealkylation, but hinders the disproportionation of toluene and ethylbenzene, through the bulky intermediate, due to the steric constraint. For large-pore zeolite, i.e., Y and Mordenite, EB disproportionation generally involves diphenylethane intermediates; the reactions undergo through bimolecular mechanisms. The activation energy of bimolecular mechanism was proved to be lower than that of monomolecular on Y zeolite. Thus, higher temperature is needed for EB disproportionation on medium-pore zeolites than on large-pore zeolites [12].

Min et al. [6] provided experimental evidence for the transition state shape selectivity in zeolite catalysts. By analyzing the reaction intermediates, it was concluded that EB disproportionation over medium-pore zeolites can differ according not only to the size of 10-ring channels but also to the existence of cavities/channels larger than 10-rings [6]. With zeolites containing 10-ring channels and 14-ring cavities, besides monomolecular, the bimolecular mechanism could also occur.

The isomerization between the DEB isomers is expected to be 1,2-shift mechanism. According to Klemm et al. [2], the reaction scheme of the isomerization of dialkylbenzene are described as linear reaction without direct conversion between *para*- and *ortho*-isomer. Olah et al. [13] conducted experiments of EB disproportionation on an aluminum chloride catalyst. They proposed a three compounds equilibration involving six rate constants. The kinetic study results indicated that the rate constants of the *ortho-para* as well as those of the *para-ortho* were equal to zero. In the study of Weiß et al. [14], the thermodynamic equilibrium of DEB isomers at 453 K, calculated from the free enthalpies of formation in the gas phase, corresponds to 54% *m*-DEB, 32% *p*-DEB, and 14% *o*-DEB. Normally, the reported distribution of DEB isomers is approximately 6:3:1 for *m*-DEB: *p*-DEB: *o*-DEB. They also reported that the kinetically favored 1,4 isomer is primary formed but with increasing residence time, the *m*-DEB becomes the predominant isomer.

The performance of the catalysts are mostly based on the acid sites and zeolite structure. EB disproportionation and transalkylation were investigated over a variety of zeolites in literature, such as Mordenite [11], USY [15], Beta [16], and ZSM-5 [17]. ZSM-5, as a MFI-type medium-pore zeolite, has interconnected channels of 10-membered rings (MR) $5.1 \times 5.5 \text{ \AA}$ and $5.3 \times 5.6 \text{ \AA}$ [18]. As mentioned previously, the transalkylation reaction mechanism changes according to the pore architecture of the zeolites. Even though Mordenite, Y, and Beta zeolites are all cataloged as large-pore zeolites, they differ considerably from each other in pore structure. Beta zeolite has two connected 12-MR channel systems with dimensions $6.6 \times 6.7 \text{ \AA}$ and $5.6 \times 5.6 \text{ \AA}$ [18]. Mordenite zeolite contains two channel sizes, but only one channel in one direction is accessible to organic molecules, the size of the channel

is $6.5 \times 7.0 \text{ \AA}$ [19]. Zeolite Y has circular channel openings that are 7.4 \AA in diameter that lead to larger cavities called supercages that are $\sim 13 \text{ \AA}$ in diameter [19]. The presence of such cavities allows more space for the formation of bulky intermediates or products, but also can act as a trap of big molecules, leading to consecutive reactions [18].

Wang et al. [20] revealed that zeolite activity in EB disproportionation decreases in the order Beta > ZSM-5 > Y \approx Mordenite, while the acidity decreases in the order ZSM-5 > Beta > Mordenite > Y. Higher activity of ZSM-5 was expected due to its higher siliceous content; however, Beta had better activity in EB disproportionation. The authors concluded that acidity is not the only controlling factor for zeolite activity. In fact, although having lower acidity, zeolite Y and Mordenite had comparable activity to ZSM-5 in disproportionation of toluene (TOL). The reaction mechanism can be another important factor that influence the activation energy and zeolite activity [20]. Nemeth et al. [21] pointed out that a catalyst containing 50 vol% Beta and 50 vol% pentasil (MTW-type zeolite) was particularly effective in converting undesired ethylbenzene isomers while still achieving a good proportion of *p*-xylene (PX) in total xylene isomers. The authors issued a patent for a liquid phase process for C₈ alkylaromatic (including EB) isomerization.

As mentioned before, the desired SMBR unit integrates the isomerization and adsorption process in a single unit for in-situ withdrawal of PX as it is formed to overcome the thermodynamic limitations in the isomerization of xylenes. The commercial aromatic streams normally contain considerable amounts of EB, 15–20% from reformat and 35–55% from pyrolysis gasoline [22]. Considering that the feed to the SMBR may contain a relatively high amount of EB and that TOL may be used as desorbent instead of *p*-DEB, it is necessary to study the disproportionation and transalkylation between C₈ aromatics and TOL under the operating conditions foreseen for the SMBR unit. The purpose of this work is focused on the side reactions that may occur in the SMBR over Beta zeolite with a SiO₂/Al₂O₃ (SAR) ratio of 35 (BEA35) under the following experimental conditions: 453, 473, and 493 K, and 2.1 MPa in liquid phase.

2. Experimental method

2.1. Materials

High purity (> 99%) ethylbenzene (EB), toluene (TOL), *p*-xylene (PX), *m*-xylene (MX), *o*-xylene (OX), and heptane were purchased from ACROS ORGANICS and used without further purification.

The catalyst was kindly supplied by Clariant in powder, in its acid form. The powder was turned into cylindrical pellets of 4 mm diameter and 2 mm height by uniaxial compression in a benchtop model tablet press (TDP 1.5) with a maximum impulsive force of 15 kN without the addition of binder. The solid was characterized through nitrogen sorption at 77 K, ammonia temperature programmed desorption (ATPD), and FTIR spectroscopy with Pyridine (see Supplementary

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