Kinetic modeling of heavy reformate conversion into xylenes over mordenite-ZSM5 based catalysts

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**Abstract**

Conversion of commercial heavy reformate into xylenes is investigated in a fluidized-bed batch reactor to develop a kinetic model. H-mordenite and H-ZSM5 based catalysts containing equal amounts of H-mordenite and H-ZSM-5 (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio: 27) were used. The SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio of H-mordenite in the catalysts was 18 and 180, which are named as MLZ and MHZ, respectively. The MLZ catalyst resulted in higher conversion of methylethylbenzenes (MEBs) and trimethylbenzenes (TMBs) and exhibited better selectivity toward xylenes due to higher acid-site concentration. Kinetic modeling was carried out using a simplified reaction network which includes: (i) dealkylation of MEBs; (ii) disproportionation of TMBs; (iii) transalkylation of TMBs with toluene; and (iv) paring reaction of tetramethylbenzenes. The results of the mathematical model closely match the experimental data, based on statistically significant estimate of the kinetic parameters, which indicates that the set of assumptions made for kinetic modeling are valid. The order of apparent activation energies, $E_{paring} > E_{dealkylation} = E_{disproportionation} > E_{transalkylation}$, can be ascribed to the relative size of the reactant molecules involved in these reactions.

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**Keywords:** Transalkylation; Kinetic modeling; Mordenite; ZSM-5; Xylenes; Heavy reformate

1. Introduction

Conversion of heavy reformate to xylenes is becoming an essential part of modern integrated refinery-petrochemical complex due to increased demand of xylenes. Multiple parallel and consecutive reactions take place during heavy reformate conversion due to the presence of a variety of aromatic compounds. A list of key reactions that occur during the heavy reformate conversion is presented in Table 1 (Ali et al., 2011a). The catalysts used for the purpose include large-pore zeolites – such as ZSM-12 (Tsai et al., 1999, 2002), faujasites (Krejci et al., 2010), zeolite $\beta$ (Čejka and Wichterlova, 2002), mordenite (Ali et al., 2011b; Tsai et al., 2002; Serra et al., 2005), SAPO-5 (Dumitriu et al., 2002), and zeolite L (Čejka et al., 2001) – and medium-pore zeolites – such as ZSM-5 (Röger et al., 1998) and NU-87 (Park and Rhee, 2000). These studies show that conversion of methylbenzenes (MEBs), trimethylbenzenes (TMBs) and heavier (C$_{10}$+) aromatics as well as product selectivities are significantly influenced by the pore dimensions and the structure of the catalysts. The highest yield of xylene was obtained with zeolites containing a combination of 10- and 12-member rings (such as NU-87) or 8- and 12-member rings (such as mordenite). Further enhancement is achieved by addition of ZSM-5 to large-pore zeolite such as mordenite and/or by incorporating metal function (Serra et al., 2005; Tsai et al., 2009; Al-Khattaf et al., 2010).

Most of the relevant published literature deals with catalyst development or parametric studies. Less attention was paid to reaction kinetics and modeling of the reaction network. Waziri et al. (2010) studied the catalytic transformations of toluene, 1,2,4-trimethylbenzene and equimolar mixture of the two compounds. They developed comprehensive kinetic models for isomerization, disproportionation and transalkylation reactions of 1,2,4-TMB and toluene. The present study focuses on the development of a kinetic model for important reactions involved in the conversion of commercial heavy reformate.

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