

Mechanistic investigations of *n*-propylbenzene disproportionation over large-pore zeolite LaNa-Y

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Introduction

Understanding the mechanisms of the disproportionation reaction of aromatic hydrocarbons over acidic zeolite catalysts remains an issue of intense study, although some of them are being commercially operated all over the world [1]. Unlike the case of toluene and ethylbenzene disproportionations [2-5], on the other hand, there is little known on the mechanisms of *n*-propylbenzene transformation, a slightly longer alkylaromatic compound. The purpose of this study is to identify the intrazeolitic organic species formed during the *n*-propylbenzene disproportionation and to gain new insights into the mechanisms of this reaction. Here we report on the observation of four different kinds of binuclear species as reaction intermediates of *n*-propylbenzene disproportionation over large-pore zeolite LaNa-Y. We have also clarified their roles on the distribution of reaction products including benzene, toluene, ethylbenzene, methylpropylbenzenes, ethylpropylbenzenes, and di-*n*-propylbenzenes.

Materials and Methods

The *n*-propylbenzene disproportionation over large-pore zeolite LaNa-Y was performed under atmospheric pressure in a fixed bed flow type apparatus at 130 °C. *n*-Propylbenzene was first purified by passing through a column filled with alumina previously activated at 250 °C to remove oxygenated aromatic impurities, and then fed into a reactor containing zeolite LaNa-Y at 8 h⁻¹ WHSV. GC-MS analysis was carried out to characterize the organic compounds entrapped inside the void spaces of the zeolite catalyst employed here. 50 mg of the used catalyst were completely dissolved in 3ml of 10% HF solutions and neutralized with K₂CO₃. The organic species from the resulting solutions were extracted by CCl₄ (Aldrich, 99.5%). The GC-MS total ion chromatograms of extracted organic phases were recorded on an Agilent 7890A gas chromatograph equipped with an Agilent 5975C mass selective detector.

Results and Discussion

Figure 1 shows the GC/MS total ion chromatogram of the CCl₄ extract of LaNa-Y after *n*-propylbenzene disproportionation at 130 °C and 8 h⁻¹ WHSV for 10 h on stream. While peaks 1, 2, 3, and 4a-c represent the reaction products, relatively weak peak 3 and very strong peak 5 correspond to 1-phenyl-1-propanone and 1-phenyl-2-propanone, respectively. Because most of oxygenated aromatic impurities in *n*-propylbenzene were removed before reaction, the organic species responsible for latter two peaks appear to be produced from the chemisorbed *n*-propylbenzene molecules in LaNa-Y during the HF dissolution. Of particular interest are peaks 11a-c, 12a,b, 13a,b and 15a-c which correspond to 1-phenyl-2-propylphenylpropane, 1-propylphenyl-2-phenylpropane, monoprolylated 1,1-diphenylpropane, and diprolylated 1,1-diphenylpropane derivatives, respectively. Further details on the identification of other GC-MS

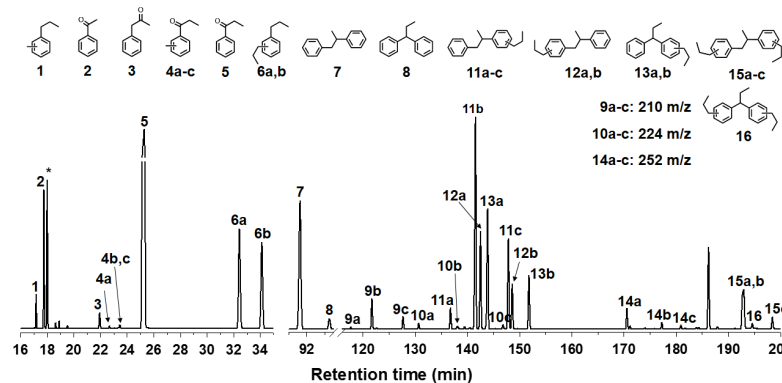


Figure 1. GC-MS total ion chromatogram of the CCl₄ extract from LaNa-Y after *n*-propylbenzene disproportionation at 130 °C and 8 h⁻¹ WHSV for 10 h, showing the assignment of each organic compound. The asterisk represents the mass signal of C₂Cl₆ produced by pyrolysis of CCl₄.

peaks and their roles as reaction intermediates of *n*-propylbenzene disproportionation will be given at the conference site.

Significance

GC-MS evidence for the build-up of monoprolylated 1,1-diphenylpropanes and diprolylated 1,1-diphenylpropanes, as well as 1-phenyl-2-propylphenyl propane and 1-propylphenyl-2-phenylpropane, as reaction intermediates of *n*-propylbenzene disproportionation over LaNa-Y is presented. On the basis of overall results of our study, a new mechanism for the zeolite-catalyzed transformation of *n*-propylbenzene will be proposed

References

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