Mechanisms of the Ethylbenzene Disproportionation: Transition State Shape Selectivity on Zeolites

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Introduction

Chemists and chemical engineers seek to utilize zeolites ‘under control’ in heterogeneously catalyzed reactions [1]. By choosing specific zeolite structures, channel and cage geometry can be varied, which can strongly influence the activity and selectivity in chemical transformations [2]. Generally, three mechanisms are described for the shape selective catalysis on zeolites: Reactant shape selectivity, product shape selectivity, and transition state shape selectivity [3]. In contrast to reactant and product shape selectivity, it is difficult to give direct experimental evidence for the transition state shape selectivity. Recently, Clark et al. used theoretical methods to investigate the transition state shape selectivity in the m-xylene disproportionation on zeolites [4].

Ethylbenzene disproportionation has attracted much attention in recent years due to the production of valuable diethylbenzene and as a standard reaction for acidity characterization by the International Zeolite Association (IZA) [5]. Most of the mechanistic studies of ethylbenzene disproportionation have been carried out with liquid Friedel-Crafts or superacidic catalysts. Up to now, the reaction intermediates have not been observed. The present study gives experimental evidence for two mechanistic pathways caused by the transition state shape selectivity during the ethylbenzene disproportionation on zeolites.

Materials and Methods

13C-enriched ethyl[α-13C]benzene was quantitatively loaded on zeolites X, Y, and ZSM-5 [6]. Subsequently, these samples were heated at desired temperatures, and in situ 13C MAS NMR investigations were performed with a 7 mm MAS probe on a Bruker MSL-400 spectrometer at the 13C resonance frequency of 100.6 MHz.

Results and Discussion

Upon zeolite Al,Na-Y/63 was heated at 443 K for 24 h, the formation of diphenylethane (D) was observed in the 13C MAS NMR spectra. This species also occurred in the ethylbenzene disproportionation on zeolite Al,Na-X/61 at 455 K. Benzene (G) was generated at the same time. However, it is difficult to be observed in 13C NMR spectra due to its non-enriched 13C atoms. Increasing the number of highly charged Al3+ cations can promote the formation of B by hydride abstraction. The hydride ions are stabilized by extra-framework aluminum cations, and SiO-Al sites stabilize the nearby B. This promotes the reaction of B with another A to form C rather than the recombination with a hydride ion back to A. The experimental observation of diphenylethane (D) in the ethylbenzene disproportionation on zeolites Al,Na-X and Al,Na-Y provides the undeniable evidence that this reaction occurs via the bimolecular reaction pathway on large-pore zeolites (Scheme 1a). Because of the significantly smaller pores of zeolite ZSM-5 (0.56 nm) compared to zeolites X and Y (0.74 nm), the bulky diphenylmethane-type transition state is too large to be formed on ZSM-5.

Upon heating zeolites ZSM-5 at 483 and 503 K for 0.5 h, the reaction starts as indicated by the formation of surface 13C-1-ethoxy groups (J), diethylbenzene (H), and oligomeric alkoxy groups by 13C CP MAS NMR. The observation of ethoxy groups hints to the monomolecular reaction pathway on medium-pore zeolites (Scheme 1b). Upon thermal treatments of ethylbenzene-loaded zeolites Al,Na-ZSM-5 and H,Na-ZSM-5 at 503 K for 0.5 h and at 573 K for 0.5 or 1 h, respectively, the oligomeric species are further transformed into aromatics, toluene, butane, propane, and ethane. In contrast, the reaction performed on large-pore zeolites is a clean process without side reactions, which is more interesting for industrial applications.

Scheme 1. Mechanisms of ethylbenzene disproportionation (a) diphenylethane-mediated bimolecular reaction pathway and (b) ethoxy-mediated monomolecular reaction pathway.

Significance

For the first time, the present work gives direct experimental evidence for the transition state shape selectivity in transalkylation reactions on microporous catalysts. In addition, the current work shows that zeolite catalysts, which are ‘fine-tuned’ in their catalytic properties, can effect the lifetime of intermediates, which is an important aspect for mechanistic investigations.

References