



1,2,4-Trimethylbenzene disproportionation over large-pore zeolites: An experimental and theoretical study



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ABSTRACT

While 1,2,4-trimethylbenzene (TMB) disproportionation is one of the potential technologies for *p*-xylene production, its reaction intermediates have been neither experimentally observed nor identified yet. Here we present GC–MS evidence that not only pentamethylated diphenylmethane (5mDPM) derivatives but also hexamethylated diphenylmethane (6mDPM) ones are serving as key reaction intermediates of 1,2,4-TMB disproportionation over large-pore zeolites. We also propose a new bimolecular diphenylmethane-mediated reaction pathway for the formation of tetramethylbenzenes (TeMBs) and xylenes over large-pore zeolites based on the GC–MS results obtained. Comparison with the GC–MS results from LaNa-Y after transalkylation reactions of three different TeMB isomers with three xylene and three TMB isomers, respectively, allows us to rationally identify most of the seven 5mDPM and three 6mDPM derivatives at their isomer level. A combination of GC–MS and DFT calculation results demonstrates that the bimolecular 1,2,4-TMB disproportionation over LaNa-mordenite, a practically one-dimensional 12-ring zeolite with regard to this reaction, is a new example of transition state shape selectivity in zeolite catalysis.

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1. Introduction

Although aluminosilicate zeolites are widely used as catalysts in a broad spectrum of petrochemical and refining processes [1–3], there is still a keen interest in understanding the mechanisms of many hydrocarbon conversion catalyzed by this important class of solid acid catalysts [4–7]. As in other areas of heterogeneous catalysis, undoubtedly, the key to elucidating the mechanisms of zeolite catalysis is the observation and identification of reaction intermediates being formed on a working catalyst under practical reaction conditions.

The transalkylation of alkylated aromatic hydrocarbons is one of the most important petrochemical technologies. 1,2,4-Trimethylbenzene (TMB) disproportionation to the three xylene and three tetramethylbenzene (TeMB) isomers is of potential industrial importance due to the high demand of *p*-xylene as a raw material mainly for the production of polyester fibers [4,5]. From an academic point of view, in addition, this special case of aromatic transalkylation is often employed as a probe reaction to estimate the pore structure of zeolites [8,9]. It has long been expected that the formation of bulky diphenylmethane-type reaction intermediates

within medium-pore zeolites such as H-ZSM-5 (framework type MFI) during 1,2,4-TMB disproportionation is severely restricted due to the spatial constraints imposed by the critical dimensions of their internal void spaces [8,10], whereas such bimolecular reaction intermediates can be formed in large-pore materials.

To our knowledge, Wang and co-workers were the first to focus on the mechanism of 1,2,4-TMB disproportionation over large-pore zeolites such as H-Y (FAU) or H-beta (*BEA) [11]. The formation of TeMB species, as well as xylene ones, at low conversion levels has led them to propose a bimolecular reaction pathway in which the formation of nine different pentamethylated diphenylmethane (5mDPM) isomers as reaction intermediates is possible. However, selectivities to TeMB and xylene isomers over both H-Y and H-beta at low conversion levels were found to be quite different from their thermodynamic equilibrium values [11]. This implies that the formation of particular 5mDPM derivatives as reaction intermediates is favored even over large-pore zeolite catalysts.

The aim of this contribution is to provide unprecedented insights into the mechanism of zeolite-catalyzed 1,2,4-TMB disproportionation. Here we present the gas chromatography–mass spectrometry (GC–MS) results from a series of used LaNa-Y catalysts in order to show that hexamethylated diphenylmethane (6mDPM) derivatives, as well as 5mDPM ones, are acting as key reaction intermediates of 1,2,4-TMB disproportionation, which could also

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be the case of other large-pore zeolites such as LaNa-beta and LaNa-mordenite (MOR). The GC-MS technique, although *ex situ* in nature, has been extensively employed to characterize the organic compounds accumulated within the void spaces of zeolite catalysts during many hydrocarbon conversions and thus to unravel their reaction mechanisms [6,12–20]. On the basis of the overall GC-MS results of our study, we were able to propose a new bimolecular reaction mechanism of 1,2,4-TMB disproportionation over large-pore zeolites. Also, we were able to accurately identify six out of the seven 5mDPM isomers and one out of the three 6mDPM ones observed in the GC-MS chromatogram from LaNa-Y after 1,2,4-TMB disproportionation by comparing with the GC-MS results from the same catalyst after transalkylations of three different TeMB isomers with three xylene and three TMB ones, respectively.

While the density functional theory (DFT) calculations are quite useful for evaluating the stability of carbenium ions in a number of zeolite-catalyzed hydrocarbon conversions and hence for elucidating the mechanisms of zeolite catalysis [21–28], on the other hand, no theoretical efforts have thus far been devoted to the disproportionation of 1,2,4-TMB. In the present study, we have carried out the relative energy calculations on all species (i.e., the reactant, reaction intermediates, transition states, and products) involved in the bimolecular pathway of this reaction over the 84T H-Y model, as well as on all nine possible 5mDPM isomers and three different 6mDPM ones embedded in the constraint-free 8T, 168T H-beta, and 68T H-mordenite (H-MOR) models, using the mixed quantum-mechanical and semi-empirical ONIOM techniques. The calculation results obtained will allow us not only to further understand the mechanism of 1,2,4-TMB disproportionation, but also to more accurately identify the types of 5mDPM and 6mDPM isomers determined by GC-MS analyses. To our knowledge, no studies have been successful for unambiguously ascertaining the reaction intermediates of any alkylaromatic hydrocarbon conversions at their isomer level.

2. Experimental

2.1. Catalyst preparation

Zeolites Na-Y (Si/Al = 2.6, Tosoh), NH₄-beta (Si/Al = 13, PQ), and Na-mordenite (Si/Al = 5, Clariant) were refluxed twice in 1.0 M NaNO₃ solutions overnight in order to ensure that they were in their complete Na⁺ form. Then, each zeolite was converted into the La³⁺-exchanged form by refluxing four times in 0.1 M La(NO₃)₃ solutions (2.0 g solid per 100 mL solution) for 6 h. Prior to use as catalysts, zeolites were granulated by pressing without a binder under a maximum pressure of 2.8×10^7 Pa, crushed, and sieved to obtain particles with a diameter of 0.2–0.3 mm.

2.2. Analytical methods

Powder X-ray diffraction patterns were collected on a PANalytical X'Pert diffractometer (Cu K_α radiation) with an X'Celerator detector. All zeolites employed in this work are highly crystalline, and no reflections other than those from each material are observed (Supplementary Fig. S1). Elemental analysis was carried out on a Jarrell-Ash Polyscan 61E inductively coupled plasma spectrometer in combination with a Perkin-Elmer 5000 atomic absorption spectrophotometer. N₂ sorption experiments were made with a Mirae SI nanoPorosity-XQ analyzer. Crystal morphology and size were determined by a JEOL JSM-6510 scanning electron microscope. Thermogravimetric analyses (TGA) were performed in air on an SII EXSTAR 6000 thermal analyzer, where the weight loss related to the combustion of organic species formed during 1,2,4-TMB disproportionation was further confirmed by differential thermal analyses (DTA) using the same analyzer. The acidic properties of all zeolites employed here were characterized by IR spectroscopy using pyridine as a probe molecule. Details of the IR measurements with adsorbed pyridine can be found in our previous papers [19,20]. After desorption at 473 K for 2 h, the concentrations of Brønsted and Lewis acid sites in zeolites were determined from the intensities of the IR bands around 1550 and 1450 cm⁻¹, respectively, using the equations of Emeis [29]. The characterization data for zeolite catalysts studied here are given in Table 1.

GC-MS analyses of the organic compounds formed on zeolite catalysts after 1,2,4-TMB disproportionation and transalkylations between three different TeMB isomers and xylene or TMB isomers were carried out following the procedure described in our previous papers [20,30]. The GC-MS total ion chromatograms were recorded on an Agilent 7890A gas chromatograph equipped with an Agilent 5975C mass selective detector, and the organic compounds extracted were identified by comparing with the NIST database [31].

2.3. Catalytic experiments

All the catalytic experiments were conducted under atmospheric pressure in a continuous-flow apparatus with a fixed-bed microreactor. Prior to the experiments, the zeolite catalyst was routinely activated under flowing N₂ (50 mL min⁻¹) at 523 K for 12 h and kept at the desired reaction temperature, allowing time for the reactant/carrier gas distribution to be stabilized. 1,2,4-TMB disproportionation was performed by feeding 1,2,4-TMB (98%, Aldrich) with a partial pressure of 12.2 kPa in N₂ into a microreactor containing 0.3 g of zeolite catalyst at a weight hourly space velocity (WHSV) of 5.2 h⁻¹. The reaction products were analyzed online in a Varian CP-3800 gas chromatograph equipped with a CP-Chirasil-Dex CB capillary column (0.25 mm × 25 m) and a flame ionization detector.

Flushing experiments, in which the 1,2,4-TMB-containing stream was replaced by a pure N₂ feed, were also performed as a

Table 1
Physicochemical properties of all zeolite catalysts employed in this study.

Catalyst	Si/Al ^a	Crystal shape and size ^b (μm)	Degree of La ³⁺ ion exchange ^a (%)	BET surface area ^c (m ² g ⁻¹)			Acidity ^d (μmol pyridine g ⁻¹)			Amount of organics deposited ^e (wt%)
				Total	Microporous	External	Brønsted	Lewis	Total	
LaNa-Y	2.6	Polygonal platelets, 0.7 × 0.7 × 0.2	78	620	550	70	289	12	301	12.8
LaNa-beta	12.5	Grains, 0.1	67	540	360	180	157	59	216	18.1
LaNa-MOR	5.0	Rods, 0.3 × 1.0	58	400	350	50	140	41	181	12.2

^a Determined by elemental analysis.

^b Determined by SEM.

^c Calculated from N₂ adsorption data.

^d Determined from the intensities of the IR bands of retained pyridine at 1545 and 1455 cm⁻¹ after desorption at 473 K after 2 h, respectively, by using the extinction coefficients given by Emeis [29].

^e The exothermic weight loss by TGA/DTA at 523–1073 K after 1,2,4-TMB disproportionation at 473 K and 5.2 h⁻¹ WHSV for 10 h on stream.

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