Reaction intermediates and mechanism of the zeolite-catalyzed transalkylation of 1,2,4-trimethylbenzene with toluene

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ABSTRACT

We report the catalytic properties of a series of large-pore (H-Y, H-beta, H-mordenite, and H-UZM-35) and medium-pore (H-NU-87, H-TNU-9, and H-ZSM-5) zeolites with different framework structures for the transalkylation of 1,2,4-trimethylbenzene (1,2,4-TMB) with toluene. H-NU-87 with intersecting 10- and 12-ring channels, but in which access to the inner part of the crystal can only occur through the 10-ring pores, was found to show a significantly higher xylene yield (40% vs. 23% at 673 K and 10 h on stream) and catalyst stability (31% vs. 17% 1,2,4-TMB conversion after 30 h on stream at 673 K) than the cage-based large-pore zeolite H-Y, the current commercial transalkylation catalyst. GC–MS analyses of organic species occluded in used zeolite catalysts reveal that the type of diphenylmethane derivatives serving as key reaction intermediates of 1,2,4-TMB-toluene transalkylation is strongly influenced by the pore architecture of the zeolite catalyst. A bimolecular diphenylmethane-mediated reaction mechanism for this transalkylation is proposed and discussed based on both experimental and theoretical results.

1. Introduction

p-Xylene is a raw material in the large-scale production of many important polymers and, particularly, of terephthalic acid for polyesters such as polyethylene terephthalate [1,2]. As a consequence, considerable advances in the *p*-xylene manufacturing process have been achieved over the past several decades [2–5]. Among the processes developed so far, transalkylation of 1,2,4-trimethylbenzene (1,2,4-TMB) with toluene is of practical importance, because it yields, in principle, two moles of xylenes from low-valued 1,2,4-TMB and toluene without producing benzene or tetramethylbenzenes [6–9]. This transalkylation has been commercialized using large-pore zeolite Y (framework type FAU), which can provide free diffusion of both reactant molecules (i.e., 1,2,4-TMB and toluene, with kinetic diameters of 6.8 and 5.9 Å, respectively) to intrazeolitic acid sites [7,10–12].

A clear understanding of the reaction mechanisms in heterogeneous catalysis, which makes it possible to find or recognize a more efficient catalyst, requires information on the nature of the transition states that connect reactants, intermediates, and products. Kaliaguine and co-workers were the first to have an interest in the possible reaction pathways of the transalkylation of 1,2,4-TMB with toluene over various zeolite catalysts, i.e., H-USY

(FAU), H-beta (*BEA), H-mordenite (MOR), and H-ZSM-5 (MFI) [13]. They suggested that this reaction could proceed via a monomolecular methyl transfer pathway and a bimolecular diphenylmethane-mediated one over medium- and large-pore zeolite catalysts, respectively. While trimethylated diphenylmethane (3mDPM) derivatives were proposed as reaction intermediates in the latter pathway, Li et al. have recently presented gas chromatography−mass spectrometry (GC–MS) evidence for the formation of dimethylated diphenylmethane (2mDPM) and tetramethylated diphenylmethane (4mDPM) species, as well as 3mDPM derivatives in the same series of zeolite catalysts, and have proposed a new bimolecular reaction pathway [14]. In their mechanism, however, the role of 2mDPM species in this reaction is not discussed at all.

In our recent study on the reaction mechanism of 1,2,4-TMB disproportionation [15], on the other hand, we have proposed that medium-pore zeolites containing large 12-ring cavities/channels accessible only through 10-ring windows may exhibit higher *p*-xylene selectivity as aromatic transformation catalysts than large-pore materials, because their smaller void spaces are more suitable for the formation of biphenyl derivatives as reaction intermediates, which may lead to the production of *p*-xylene. In the present study, we report that H-NU-87 (NES), a zeolite with such an aforementioned pore architecture, shows a higher xylene yield and better catalyst stability in the transalkylation of 1,2,4-TMB with toluene than H-Y, the current commercial catalyst for this

reaction. We were also able to identify the roles of all of the 2mDPM, 3mDPM, and 4mDPM species clearly by analyzing the GC–MS results of large-pore (H-Y, H-beta, H-mordenite, and H-UZM-35 (MSE)) and medium-pore (H-NU-87, H-TNU-9 (TUN), and H-ZSM-5) zeolites, allowing us to propose a more reliable bimolecular mechanism than the previously reported reaction pathway [14]. The validity of our mechanism has been further demonstrated by calculating the relative energies of reactants, reaction intermediates, and transition states in the structure models of the zeolite catalysts studied here, using the mixed quantum-mechanical and semiempirical ONIOM method.

2. Experimental

2.1. Catalyst preparation and characterization

H-Y (Si/Al = 15) and NH$_4$-beta (Si/Al = 13) were obtained from PQ, and H-mordenite (Si/Al = 10) and NH$_4$-ZSM-5 (Si/Al = 14) were purchased from Tosoh. All these zeolites were refluxed twice in 1.0 M NH$_4$(NO$_3$)$_3$ solutions (2.0 g solid per 100 mL solution) for 6 h followed by calcination at 823 K for 4 h in order to ensure that they were completely in the proton form. UZM−35 (Si/Al = 9), NU-87 (Si/Al = 25), and TNU-9 (Si/Al = 18) were synthesized, converted into their proton forms, and characterized by powder X-ray diffraction, scanning electron microscopy, elemental analysis, and N$_2$ adsorption as described in our previous work [16,17]. 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.

The acidic properties of zeolite catalysts were characterized by IR spectroscopy using pyridine as a probe molecule. Details of the IR measurements with adsorbed pyridine can be found elsewhere [18]. Thermogravimetric analysis (TGA) was performed in air on an SII EXSTAR 6000 thermal analyzer, where the weight loss related to the combustion of organic species formed on each zeolite catalyst during 1,2,4-TMB-toluene transalkylation was further confirmed by differential thermal analysis (DTA) using the same analyzer. The characterization data for zeolite catalysts examined in this work are given in Table 1. GC–MS analyses of the organic compounds formed within zeolite catalysts after transalkylation of 1,2,4-TMB with toluene were carried out by procedures reported in the literature [18,19]. 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 them with the NIST database [20].

2.2. Catalysis

Transalkylation of 1,2,4-TMB with toluene was performed at atmospheric pressure in a continuous-flow apparatus with a fixed-bed microreactor. Prior to the experiments, the zeolite catalyst was activated under flowing N$_2$ (50 mL min^{-1}) at 723 K for 2 h and kept at the desired reaction temperature, allowing time for the reactant/carrier gas distribution to be stabilized. Then a reactant stream containing an equimolar mixture of 11.1 kPa 1,2,4-TMB (98%, Aldrich) and 11.1 kPa toluene (99%, Aldrich) in N$_2$ as a balance gas was passed over the zeolite catalyst at a desired reaction temperature for 10 h with a weight hourly space velocity (WHSV) of 5.2 h^{-1}. Both 1,2,4-TMB and toluene were used without further purification, and if required, WHSV was increased to 15.5 h^{-1}. The reaction products were analyzed on line 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 for 10 h, and the first analysis was done after 5 min on stream.

Flushing experiments, in which the reactant-mixture-containing stream was replaced with a pure N$_2$ feed, were conducted at a given temperature as a function of time. Before these experiments, the catalyst was reacted with 1,2,4-TMB and toluene at 403 K for 10 h, cooled quickly to room temperature, and divided into a series of batches in exactly the same amount (50 mg). Then each batch was flushed in a pure N$_2$ stream (40 mL min^{-1}) at 403 K for times ranging from 0 to 160 min. The flushed catalyst was handled with exactly the same HF dissolution procedures given elsewhere [18,19] in order to follow the evolution of the organic compounds accumulated within zeolite pores with increasing flushing time.

2.3. Computational methods

The 84T, 168T, 112T, 64T, 62T, and 72T cluster models were extracted from the crystallographic data on H-Y, H-beta, H-UZM-35, H-TNU-9, H-NU-87, and H-ZSM-5, respectively, which are available from the Structure Commission of the International Zeolite Association [21], and applied to calculate the relative energies of all species (i.e., reactants, reaction intermediates, transition states, and/or products) that could be formed during the bimolecular transalkylation of 1,2,4-TMB with toluene. Here the calculations on H-mordenite were not performed because the contribution of the bimolecular pathway to the overall catalytic action of this large-pore zeolite was negligible (see below). The theoretical hybrid model, i.e., a combination of B3LYP/6-31G(d,p) and ωB97XD/6-31G(d,p)) B3LYP theory with the semiempirical

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

Catalyst	Si/Al[a]	Crystal shape and size (µm)[b]	BET surface area (m^2 g^{-1})[c]			Acidity (µmol pyridine g^{-1})[d]			Amount of organics deposited (wt.%)[e]
			Total	Microporous	External	Brønsted	Lewis	Total	
H-Y	15	Polygonal platelets, 0.7 × 0.7 × 0.2	800	690	110	113	18	131	10.8
H-beta	13	Grains, 0.1	540	360	180	116	59	175	11.5
H-mordenite	10	Rods, 0.3 × 1.0	620	570	50	124	14	138	18.7
H-UZM-35	9	Platelets, 0.2 × 0.05	470	380	90	154	38	192	11.9
H-NU-87	25	Rods, 0.3 × 1.0	460	420	40	109	19	128	9.8
H-TNU-9	18	Rods, 0.3 × 1.0	530	480	50	143	16	159	13.4
H-ZSM-5	14	Rods, 0.3 × 1.0	390	330	60	158	17	175	10.7

[a] Determined by elemental analysis.
[b] Determined by SEM.
[c] Calculated from N$_2$ 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 [18]. The acidity of H-mordenite may be underestimated here because pyridine cannot diffuse into its small 8-ring channels.
[e] The exothermic weight loss by TGA/DTA at 523–1073 K after transalkylation of 1,2,4-TMB with toluene at 673 K and 5.2 h^{-1} WHSV for 10 h on stream.