



Contents lists available at ScienceDirect

## Applied Catalysis B: Environmental

journal homepage: [www.elsevier.com/locate/apcatb](http://www.elsevier.com/locate/apcatb)

## Dehydration of 1,3-butanediol to butadiene over medium-pore zeolites: Another example of reaction intermediate shape selectivity

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## ARTICLE INFO

## Keywords:

1,3-Butanediol dehydration  
Medium-pore zeolites  
Framework topology  
Reaction intermediate shape selectivity

## ABSTRACT

Here we compare the catalytic properties of the proton form of 11 medium-pore zeolites, with different framework topologies and/or compositions for the dehydration of biomass-derived 1,3-butanediol at 300 °C under excess water conditions ( $\text{H}_2\text{O}/1,3\text{-butanediol} = 45$ ). It was found that high-silica H-ferrierite ( $\text{Si}/\text{Al} = 130$ ) with intersecting 10- and 8-ring channels exhibits the highest butadiene yield, together with the best durability, among the zeolites tested. Due to its highly inactive nature, however, 3-buten-1-ol, one of the butenol reaction intermediates in 1,3-butanediol dehydration, also remained a major by-product. IR spectroscopy with adsorbed 3-buten-1-ol shows that intramolecularly hydrogen-bonded 3-buten-1-ol exists predominantly in H-ZSM-5 with two intersecting 10-ring channels, while the one with no intramolecular hydrogen bonding is another species found not only in H-ferrierite but also in the one-dimensional 10-ring zeolite H-ZSM-22. By combining both experimental and theoretical results, we conclude that 1,3-butanediol dehydration over medium-pore zeolites may constitute another example of reaction intermediate shape selectivity.

## 1. Introduction

Biomass-derived chemicals pave the environmentally friendly ways of producing various chemical building blocks owing to their carbon neutrality [1–3]. This has also been urged by disastrous climate change, as well as the switch of cracker feeds from naphtha to natural gas with the enhanced affordability of shale gas [1,4]. The so-called shale gas revolution, especially in North America, has triggered a deficit of  $\text{C}_3\text{--C}_4$  olefins including butadiene, the most basic and important conjugated diene, which is widely used as a building block for the manufacture of synthetic rubbers, such as polybutadiene, styrene-butadiene rubber and acrylonitrile-butadiene-styrene copolymers [5,6]. Since commercial butadiene is mainly obtained as a by-product of ethene production from naphtha cracking [4], their sustainable production from renewable alternative feedstocks is of prime importance.

One of the traditional alternatives to producing butadiene is the acetylene-based route, which was developed in Germany during the World War II but abandoned with the advent of low-cost naphtha cracking technology [7–9]. There is a general consensus that this process involves acetylene hydration to acetaldehyde which can then be condensed and further reduced to 1,3-butanediol (BDO) that is finally dehydrated to butadiene. Because most  $\text{C}_4$  alcohols including three BDO isomers (i.e., 1,3-, 1,4-, and 2,3-BDOs) are obtained from the biomass

fermentation process at commercial scale [10–12], the acid-catalyzed dehydration of BDO can be regarded as another green alternative route to butadiene. Since 2,3-BDO pinacol rearrangement and 1,4-BDO cyclodehydration render 2-butanone and tetrahydrofuran as major products, respectively, 1,3-BDO has particular relevance for butadiene production [13].

Given the great success of the large-pore zeolite Y (IZA code FAU) in various improved forms as fluidized catalytic cracking catalysts since 1964 [14], it is not surprising that zeolites and zeolite-like materials have had a firm place in the modern oil refinery and petrochemical industries [15]. One of the intrinsic characteristics of zeolite catalysts is their uniformly defined pore architecture which can strongly affect the selectivity of the reaction products. Since the seminal proposal by Weisz and co-workers [16,17], as a consequence, three theories of shape selectivity in zeolites, i.e., reactant, product, and transition-state shape selectivities [17,18], have been well established. To develop new process concepts, as well as to improve current catalytic processes, in addition, other various theories, encompassing reaction intermediate shape selectivity, pore mouth catalysis, key-lock mechanism, molecular traffic control, the window effect, and the nest effect [18–20], have been proposed.

While many different types of solid acids, e.g., phosphate-based catalysts, mixed metal oxides, amorphous silica-alumina, etc., have

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Received 3 June 2020; Received in revised form 6 August 2020; Accepted 13 August 2020

Available online 17 August 2020

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