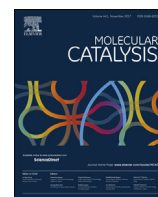




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Research Paper

Active site structure of a lithium phosphate catalyst for the isomerization of 2,3-epoxybutane to 3-buten-2-ol

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ABSTRACT

Basic lithium phosphate (B-LPO) catalyst selectively produces unsaturated alcohols from epoxides. The catalytic activity of B-LPO is known to originate from appropriate acidic-basic properties, but no details were available on the structure of the active site. In this study, experimental methods and DFT calculations were performed in an attempt to identify the active surface structure of B-LPO for the isomerization of 2,3-epoxybutane to 3-buten-2-ol. The experimental results showed that exchanged Na ions in B-LPO suppressed the formation of an acid-catalyzed by-product (methyl ethyl ketone). In addition, H₂O had a negative effect on the formation of 3-buten-2-ol due to the preoccupation of the active site. DFT calculations in conjunction with these experimental observations showed that the most plausible active surface for the formation of 3-buten-2-ol is the (001) surface of LPO whose acidic proton is exchanged with Na atom. On this surface, the under-coordinated Li atoms and the surface P=O groups are exposed, and these play a role in activating the C–O bond of an epoxide ring, and in receiving a proton from the terminal carbon, respectively.

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1. Introduction

With depletion of fossil resources and a growing demand for environmentally benign production technologies, the catalytic conversion of biomass is expected to replace conventional petrochemical processes [1]. 2,3-butanediol is one of important biomass-derived feedstocks, and is a potential source for production of valuable C4 chemicals [2]. Catalytic dehydration of 2,3-butanediol is an effective way in that various chemicals such as methyl ethyl ketone [3], 3-buten-2-ol (BO) [4,5], 2,3-epoxybutane (EB) [6], and 1,3-butadiene [7,8] can be produced. Among these products, 1,3-butadiene is practically important chemical in the synthesis of polymers, including ABS, NBR, and SBR polymers. In this regard, production of 1,3-butadiene from 2,3-butanediol has been extensively studied [7,8].

Sato et al. reported the direct production of 1,3-butadiene from 2,3-butanediol using rare-earth metal oxides [7]. Sc₂O₃ was the

best catalyst that showed 88% yield of 1,3-butadiene. They also found that BO was an intermediate chemical during the formation of 1,3-butadiene. The same group also reported that ZrO₂ based catalyst were effective to the production of BO from 2,3-butanediol [4,5]. Filimonov et al. also reported the direct formation of 1,3-butadiene using silica-supported sodium phosphates [8]. They observed that contact time and Na/P ratio considerably influenced product distribution. As similar to the report by Sato et al., BO was detected as an intermediate for the formation of 1,3-butadiene.

Dehydrative epoxidation of 2,3-butanediol using Cs/SiO₂ catalyst can be another alternative way for the production of 1,3-butadiene [6]. This reaction produces EB from 2,3-butanediol, and the product can be isomerized into BO. There are several reported catalysts for the selective isomerization of epoxides into unsaturated alcohols, such as Au/TiO₂ (liquid-phase isomerization) [9,10] and lithium phosphates (gas-phase isomerization) [11–13]. In the isomerization of epoxides, it was commonly reported that the acidic-basic properties of a catalyst determine catalytic performance [9–14].

Teranishi et al. studied the effects of acidic-basic properties on the isomerization of propylene oxide [11,14]. When they utilized acidic zeolites, only carbonyl compounds including acetone and propionaldehyde were produced [14]. They also found that the

Abbreviations: B-LPO, basic lithium phosphate; N-LPO, neutral lithium phosphate; EB, *trans*-2,3-epoxybutane; BO, 3-buten-2-ol.

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