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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, H_2O 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.

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]. Sc_2O_3 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 ZrO_2 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/SiO_2 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/TiO_2 (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

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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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ratio of acetone to propionaldehyde was proportional to the acidic strength of a catalyst.

In contrast, lithium phosphate (Li_3PO_4, hereafter LPO)-based catalysts were capable of producing allyl alcohol [11]. Stoichiometric LPO exhibited rather poor selectivity toward allyl alcohol (17%), but, when LPO was synthesized with the addition of other alkali-metals (Na or K), it showed higher selectivity (~86%) as well as higher activity. In particular, Li_2NaPO_4, so-called basic lithium phosphate (B-LPO), showed the best performance. The LPO catalysts that contained alkali metals possessed stronger basic sites and weaker acidic sites than the stoichiometric LPO, which indicated that basic sites are essential for the formation of allyl alcohol. The authors also performed reaction tests by titrating acidic or basic sites with pyridine or dichloroacetic acid, respectively, and thereby found that both acidity and basicity were required for the formation of allyl alcohol.

Zhong et al. reported a similar tendency whereby basic LPO showed a catalytic performance that was higher than that of stoichiometric LPO [12]. They also studied the effect of precursors for lithium, sodium, and phosphate on the morphology and catalytic properties of basic LPO [13]. Lithium hydroxide and sodium phosphate were more appropriate precursors, as the synthesized LPO showed higher performance thanks to a crystallinity and a surface area that was better and higher, respectively, than that of the others tested.

Previous studies helped explain the isomerization of epoxides in terms of acid-base catalysis. However, no studies regarding surface structures and the roles of the surface moieties have been performed, which limits a fundamental understanding of the catalysis in the reaction. The identification of active surface structures would be helpful to design improved catalyst for this reaction.

Herein, we rationally identified the active surface of an LPO catalyst for the isomerization of EB to BO, and proposed the roles of the surface moieties during catalysis. Basic and neutral lithium phosphates (B-LPO and N-LPO, respectively) were compared to identify characteristics of the active catalytic materials. We performed several experiments including catalytic activity tests, structural characterization, and acidic-basic characterization. Based on the experimental evidences, theoretical DFT calculations were carried out to identify the active surface of LPO. The presence of the identified active surface was also confirmed via FT-IR analyses. Finally, the roles of the surface moieties on the active surface structure were proposed, based on the optimized geometry for adsorption of EB. These results will be helpful in the design and synthesis of more active catalysts for these types of reactions.

2. Experimental and theoretical methods

2.1. Preparation of catalysts

Basic lithium phosphate (B-LPO) was prepared via precipitation. First, 1.82 g of sodium phosphate monobasic (0.015 mol, NaH_2PO_4, Sigma-Aldrich) and 1.28 g of lithium hydroxide monohydrate (0.030 mol, $LiOH{\cdot}H_2O$, Sigma-Aldrich) were separately dissolved in 15 ml and 10 ml of deionized water, respectively. The former solution (NaH_2PO_4) was transferred to a 100 ml round-bottom flask, and was then heated to 40 °C with stirring. The aqueous solution of $LiOH{\cdot}H_2O$ was then added drop-wise with vigorous stirring. A white precipitate was immediately formed when the solution was added. After complete injection of the solution, the mixed solution was aged for 24 h at 40 °C. The white precipitates were isolated on a filter, washed three times with 200 ml of de-ionized water, and dried overnight at 343 K. Calcination of the dried precipitates was conducted at 673 K (5 K/min of ramping speed) for 6 h. The resultant powder was ground and sieved to retain aggregates below 200 μm prior to a use in a catalytic reaction.

The preparation of neutral lithium phosphate (N-LPO) followed a procedure similar to that of B-LPO, except for the source of phosphate. First, 1.28 g of lithium hydroxide monohydrate (0.030 mol, $LiOH{\cdot}H_2O$, Sigma-Aldrich) was dissolved in 10 ml of deionized water, and then the solution was heated to 60 °C with stirring. The solution was neutralized via the drop-wise injection of 0.7 M H_3PO_4 aqueous solution with vigorous stirring. The neutralized solution was aged for 24 h at 60 °C. The remaining procedures were identical to those for B-LPO preparation: filtration, washing, drying, calcination, and grinding.

2.2. Catalytic activity tests

Catalytic reactions for the isomerization of *trans*-2,3-epoxybutane (hereafter EB, purchased from Alfa Aesar (97%)) were performed on a fixed-bed quartz reactor with a thermocouple well. A K-type thermocouple was placed on the thermocouple well to measure the reaction temperature, and the reactor was externally heated using an electric furnace. A varied amount of catalyst (3–50 mg) was used in the catalytic reaction to maintain a conversion level lower than 20%. The reactor was heated to the desired temperatures with a ramping rate of 10 °C/min and was maintained for 30 min with a flow of dry N_2 (99.999%, 30 cm3 min^{-1}). An aqueous solution of the reactant was then injected using a liquid syringe pump (Cole-Palmer 74900 series) into a pre-heating zone, which was maintained at 200 °C. The values for the concentration of the reactant solution and dry N_2 flow rate were varied to control the partial pressure of H_2O (0–62 kPa) while maintaining other conditions in a constant state: total flow rate (51 sccm) and the partial pressure of EB (0.9 kPa). In the reaction condition, there were no mass transfer limitations (Mears criterion for external mass transfer limitation, and Weisz-Prater criterion for internal mass transfer limitation; see Supporting information). Product gases were cooled using a helix-type condenser, and liquefied contents were collected hourly in a sample tube containing deionized water. Acetonitrile was used as an external standard for quantification. The products were analyzed using gas chromatography (Younglin ACME 6100 instrument) equipped with a FID detector and an Rtx®-VRX capillary column (Restek, cat. # 19316). The data acquired after 2 h of reaction time were used to compare the activity of the catalysts.

2.3. Characterization

High-resolution transmission electron micrograph (HR-TEM) images were obtained using a JEOL JEM-3010 microscope with an acceleration voltage of 300 kV. The X-ray diffraction (XRD) patterns were obtained using a Rigaku D-MAX2500-PC powder X-ray diffractometer with Cu Kα radiation (1.5406 Å) in an operating mode of 50 kV and 100 mA. The crystallite sizes were calculated based on peaks at 16.8° ((010) plane) and 36.9° ((002) plane) using the Scherrer equation. N_2 adsorption-desorption analyses were carried out using a Micromeritics ASAP-2010 instrument. The specific BET surface area was calculated at $P/P_o = 0.1–0.2$.

X-ray photoelectron spectroscopy (XPS) was performed on a KRATOS AXIS electron spectrometer with Mg Kα radiation. The binding energies were corrected using C 1s as an internal standard (284.5 eV). The peaks were fitted by mixed Gaussian-Lorentzian functions (10% Lorentzian) with subtraction of the Shirley-type background using a XPS peak-fitting program (XPSPEAK 4.1). The ^7Li and ^{31}P magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra of the samples were recorded on a Bruker AVANCE 400 WB (400 MHz) spectrometer operated at frequencies of 156