Elucidation of Active Surface and the Roles of Surface Moieties 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 is well known catalyst for the isomerization of epoxides to unsaturated alcohols, but no details were available on the structure of the active site. In this work, active surface structure for the isomerization of 2,3-epoxybutane to 3-buten-2-ol was identified based on experimental and theoretical methods. The identified active surface contains under-coordinated Li atoms and apical oxygen of phosphate group, which play a role of activating C-O bond of 2,3-epoxybutane and of receiving proton from terminal methyl group.

Keywords: Epoxide, unsaturated alcohol, isomerization.

1. Introduction

Epoxides are important intermediate chemicals in industrial chemical processes [1]. Unsaturated alcohol is an important chemical that can be produced from epoxides via isomerization with ring opening [2]. In this reaction, the catalyst choice is particularly important as unstable epoxides tend to transform to more stable carbonyl compounds, such as ketones and aldehydes, rather than to unsaturated alcohols.

Basic lithium phosphate (B-LPO) catalyst is able to selectively produce unsaturated alcohols from epoxides, but no studies has reported regarding surface structures and the roles of the surface moieties. In this work, the active surface of an B-LPO catalyst for the isomerization of 2,3-epoxybutane (EB) to 3-buten-2-ol (BO) was identified based on experimental and theoretical methods, and the roles of the surface moieties were proposed. Catalytic activity tests, physico-chemical characterization were performed, and DFT calculations were carried out to identify the active surface structure of B-LPO. Characteristics of the identified active surface agreed well with the experimental observations. Based on the DFT-optimized geometry for adsorption of EB, plausible roles of the surface moieties were proposed.

2. Experimental

B-LPO was prepared via precipitation method. As-prepared precipitates were calcined at 673 K for 6 h. Neutral lithium phosphate (N-LPO) was also prepared via the same method, but without the presence of Na source. The calcination temperature was identical to that of B-LPO.

Catalytic activity tests were performed on a fixed-bed quartz reaction. Total flow rate was 51 sccm and the partial pressure of EB was 0.9 kPa. Product gases were cooled and were collected in sample tube. The products were analyzed using gas chromatography equipped with a FID detector.

HR-TEM were performed using a JEOL JEM-3010 microscope. XRD patterns were obtained using Rigaku D-MAX2500-PC powder X-ray diffractometer. XPS was performed on Kratos AXIS electron spectrometer. DFT calculations were performed using the Vienna *ab initio* simulation package (VASP) [3].

3. Results and discussion

TEM images of both catalysts showed agglomerates of rod-shaped crystallites. The XRD patterns for the two catalysts matched well with patterns of the Li_3PO_4 with the $Pmn2_1$ space group (PDF#25-1030). Neither peak shifts nor additional peaks were observed for both catalysts. Crystallite sizes for B-LPO was smaller than that for N-LPO, as evidenced by broader peaks. The specific BET surface areas were 23.5 and

3.4 m^2/g for B-LPO and N-LPO, respectively. In XPS results, compositions of elements for B-LPO and N-LPO were almost identical, but only B-LPO contains small amounts of Na ions. The binding energy of Na ions in B-LPO was similar to that of Na-exchanged zeolites rather than that of Na_3PO_4, which indicated that the role of Na ions was elimination of strong acidic sites.

B-LPO showed a 6-fold higher activity (49.3 vs. 8.3 $mmol_{EB}/g_{cat}\cdot h$) as well as higher selectivity toward BO (94 vs. 53%). The higher activity can be attributed to the higher surface area of B-LPO. The higher selectivity can be related to the presence of Na ions, which suppress the strong acidic sites of lithium phosphate surface.

In the DFT-optimized geometry for the adsorption of EB on the active surface of B-LPO, the important moieties were under-coordinated Li atoms and the apical oxygen of phosphate group. The under-coordinated Li atoms strongly binds the epoxy oxygen of EB molecule, and activates C-O bonds of an epoxide ring. The apical oxygen atom interacts with a hydrogen atom of terminal methyl group of EB. This presumably receives a proton from the EB molecule upon the formation of a C=C double bond, and then transfer the proton to the epoxy oxygen.

4. Conclusions

Based on the experimental and theoretical results, the active surface structure and the roles of surface moieties of B-LPO catalyst for the isomerization of 2,3-epoxybutane to 3-buten-2-ol was proposed. The under-coordinated Li sites activate the C-O bond of an epoxide ring, and the surface P=O moieties receive a proton from the terminal methyl of EB.

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