Production of 1,3-butadiene from 2,3-butanediol using cesium oxide supported silica catalyst

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Introduction

The catalytic conversion of biomass to value-added chemicals has been raised as an alternate to conventional petrochemical processes.[1] 1,3-butadiene (BDE) is one of essential monomers for polymer synthesis, and has been solely produced via petrochemical process. Production of BDE from biomass derived feedstock is of great importance in that a renewable resource is utilized as opposed to a petrochemical process. 2,3-butanediol (BD) has been recognized as attractive biomass derived source for BDE production[2] because BD can be converted to BDE through elimination of two water molecules. However, a heterogeneous catalytic process for the production of BDE from BD has been hampered because unreactive methyl ethyl ketone (MEK) and isobutyraldehyde (IBA) were formed via conventional acid-catalyzed dehydration of BD.

In this study, we demonstrate a heterogeneous catalytic process for the production of BDE from BD via a novel type of dehydration which yields 2,3-epoxybutane (EB) from BD. We refer to the novel dehydration as ‘dehydrative epoxidation’. The proposed catalytic process is composed of 3 steps: First is dehydrative epoxidation of BD to EB, second is isomerization of EB to 3-buten-2-ol (BO), and last is dehydration of BO to BDE.

Materials and Methods

Cs/SiO₂ catalyst (10 wt.% of Cs₂O) was prepared by the incipient wetness impregnation method. Basic lithium phosphate (Li₃PO₄) was prepared by precipitation method. Aluminosilicate, mesostructured (Al-MCM-41, Sigma-Aldrich) was used as received. A fixed-bed quartz reactor was used to perform catalytic reaction tests. Products were analysed by gas chromatography.

Results and Discussion

We recently found that gas-phase reaction of 2,3-butanediol (BD) over Cs/SiO₂ catalyst resulted in the formation of 2,3-epoxybutane (EB, Figure 1). Importantly, the formed EB is much reactive than the products of conventional acid catalyzed dehydration (MEK and IBA), and can serve as a bridging intermediate between BD and BDE. However, EB as it stands is not suitable precursor for the selective production of BDE because low BDE yield of 19 % was obtained when EB was reacted over acidic Al-MCM-41 catalyst at 250 °C. It was appeared that BO is much appropriate in this purpose as reaction of BO over the same catalyst showed much higher selectivity (97 %). Hence, an additional isomerization step for the transformation of EB into BO is required for the selective BDE production. We found that this transformation can be performed by a basic lithium phosphate catalyst. When cis-EB was reacted over the catalyst, it was selectively converted to BO (S = 75%), and small quantity of racemic-BD and trans-EB were produced. The reaction of trans-EB did not produce BD and cis-EB, and showed higher selectivity toward BO (92 %). On the basis of these results, it can be concluded that sequential catalytic process consisting of dehydrative epoxidation, isomerization, and acid catalyzed dehydration can provide the highly selective production of BDE from BD.

Significance

These findings can serve the alternative way for the production of 1,3-butadiene which is an important building block chemical for polymer synthesis and organic chemistry.

Figure 1. a) Dehydration of 2,3-butanediol over Cs/SiO₂ catalyst and b) acid catalyzed dehydration of 2,3-epoxybutane and 3-buten-2-ol over acidic Al-MCM-41 catalyst.

Figure 2. Proposed catalytic process for the selective production of 1,3-butadiene from 2,3-butanediol

References