



Liquid-phase dehydration of propylene glycol using solid-acid catalysts

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ABSTRACT

In this work we combine experiments with Density Functional Theory (DFT) calculations to investigate the heterogeneous dehydration of propylene glycol. The reactions were carried out with pure, liquid propylene glycol over MFI-framework zeolite catalysts or the mesoporous sulfonic-acid resin Amberlyst 36Dry. When Amberlyst 36Dry was used, propylene glycol dehydrated to form propionaldehyde with 77% selectivity. All of the propionaldehyde further reacted with propylene glycol to form a cyclic acetal. The final products consisted of 78% acetal, 13% dipropylene glycol, and the remaining 9% was composed of acetone and a cyclic ketal formed from acetone. The zeolite catalysts demonstrated significantly higher selectivity toward dipropylene glycol compared to Amberlyst 36Dry. Furthermore, the zeolite had a lower conversion to cyclic acetals, improving the selectivity toward C3 products, acetone and propionaldehyde. DFT calculations confirmed that propionaldehyde is the favorable product in both catalysts, since it can be formed either through dehydration of the secondary hydroxyl group or via dehydration of the primary hydroxyl group with a concerted pinacol rearrangement. However, in the case of zeolites, the cyclic acetals experience steric hindrance since their size is comparable to that of the zeolite pores. Thus we argue that the cyclic acetals produced over the zeolite catalyst were formed homogeneously from the C3 products which diffused out of the zeolite pores.

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1. Introduction

Increasing the market viability of biomass-derived fuels and chemicals is an essential step for reducing the dependence of our society on crude oil. One such fuel is biodiesel, which can be produced by biomass-derived sources (i.e. fatty acids), a process which forms surplus amounts of crude glycerol as a side-product. As a result, glycerol can be utilized as a renewable, low-cost feedstock for the production of fuels and chemicals [1,2]. A detailed overview of the current trends of glycerol processing can be found in the literature [3]. Propylene glycol (1,2-propanediol) is an interesting intermediate produced by glycerol hydrogenolysis that can be further processed into other specialty chemicals. Furthermore, it can serve as a model polyol since it is the simplest molecule containing both a primary and a secondary hydroxyl group.

In particular, propylene glycol dehydration can lead to the formation of propionaldehyde or acetone. Propionaldehyde is

primarily produced from 1-propanol and thus, ultimately from propylene, a fossil-fuel feedstock. It can be further transformed into several other C3 compounds and finds use in production of pharmaceuticals and plastics [4]. Acetone is a commodity chemical produced either as a co-product in the cumene process for the synthesis of phenols or by dehydrogenation of isopropyl alcohol, both of which begin with fossil-fuel feedstocks [5]. Acetone is primarily used as a solvent or as an intermediate for the production of methylmethacrylate or bisphenol-A [5]. In addition, Dumesic and co-workers have proposed [6] a process for converting sugars to alkanes which requires 5-hydroxymethylfurfural (produced renewably from glucose [7]) and acetone. Thus, in addition to its current industrial use, the selective dehydration of propylene glycol to acetone could provide a source of renewable acetone needed for the conversion of sugars to alkanes.

Diol dehydration chemistry has been summarized by Bartók and Molnár [8]. Despite the extensive studies on diol dehydration, only a limited number of studies focus on propanediol. Bucsi et al. studied the dehydration of 1,2-diols over Nafion-H and zeolite NaHX at 175 and 250 °C, respectively [9]. Nafion-H was more active than NaHX at 1 g/g-h weight hourly space velocity (WHSV). In the case of Nafion-H, the diol converted primarily to propionaldehyde (74%) and the cyclic acetal species 2-ethyl-4-methyl-1,3-dioxolane (19%), which

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