Catalytic Glycerol Conversion into 1,2-Propanediol in Absence of Added Hydrogen: Bifunctional catalysis with Pt/NaY

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Introduction

1,2-Propanediol is a bulk chemical intermediate used for the production of unsaturated polyester resins, as an industrial solvent and antifreeze, an approved additive in foods, cosmetics and pharmaceutical preparations, and as a lubricant for food machinery. Whereas the industrial route involves hydration of propene oxide, glycerol from renewable origin seems to be an attractive source for sustainable future production of chemical intermediates. Glycerol is known to react with H₂ to form 1,2-propanediol (PD) and water via consecutive dehydration and hydrogenation reactions. Unfortunately, literature results imply the use of expensive bimetallic or petrochemically derived H₂.³ H₂ originating from reforming of natural gas or petroleum fractions, makes the process dependant on fossil carbon. The catalytic system discussed below is assumed to generate an autogenous reducing environment, allowing in-situ transformation of glycerol into 1,2-propanediol.³ The reducing environment for hydrogenation is generated via aqueous reforming. CO₂ is a side-product, and precursor for the dehydration catalyst.

Materials and Methods

Reactions are carried out in high pressure autoclaves. The catalysts (supported and exchanged Pt on NaY, γ-alumina) were synthesized from known procedures. Pt on carbon was commercial. The catalyst was characterized with XRD, MAS NMR and ESEM. Product analysis was performed using common GC techniques.

Results and Discussion

Results from batch experiments in inert atmosphere devoid of any added H₂ will be presented. Interestingly, on increasing glycerol conversion, the carbon selectivity for liquids and in parallel to propanediol, increases significantly. This indicates that glycerol carbon conversion to gaseous products decreases in time. In qualitative terms it seems that during the initial reaction period, some feed molecules undergo steam reforming and consecutive water gas shift. Liquid reforming is well-established now.² During the initial stage, mainly gaseous compounds are produced. Hydroxyacetone is probably the precursor of PD, as selectivities decrease and increase with conversion, respectively. This was also confirmed substituting hydroxyacetone for glycerol as feed. With added H₂ and hydroxyacetone as feed, initially high conversion and PD selectivity can be achieved, indicating that i., the initial gas formation period disappears upon external addition of H₂ and ii., PD can be formed by Pt-catalyzed hydrogenation of hydroxyacetone.

Importantly, the new catalyst (2.7Pt/NaY) is prepared by impregnation of NaY zeolite with Pt-tetrammine chloride salt, followed by dehydration, calcination and reduction. In contrast to ion-exchanged zeolite (Pt-NaY), such catalyst does not contain any residual acidity. Via the Scherrer equation, it was found that a significant amount of Pt is present as extra-framework particles of about 42 nm. XRD as well as ESEM on exchanged Pt-NaY shows absence of large metal clusters. It is clear that after ion exchange and further catalyst activation, the ion-exchanged zeolite is acid and contains intra-framework Pt.

Comparison of the carbon selectivity at short reaction time and relatively low conversion is done for the ion exchanged and impregnated samples. The decreased liquids as well as PD selectivity for the ion-exchanged catalyst shows that the presence of small intra-crystalline Pt clusters is at the basis of extensive gas formation via liquid reforming. On the large extra-framework Pt particles on the impregnated sample, the hydrogenolysis reaction seems to be more specific, yielding less gas (and more PD via hydrogenation of hydroxyacetone). As the glycerol dehydration into hydroxyacetone is probably Brønsted-acid catalyzed, its occurrence on the non-acidic Pt/NaY requires some clarification. Some of the CO₂ formed via liquid reforming will dissolve in the aqueous reaction medium, generating H₂CO₃ which will dissociate in free protons. NaY will accept most of these protons via ion exchange with Na+, thus generating a partially exchanged H-NaY. MAS NMR characterization of this material will be shown. The balance between the two types of sites, viz. protons and metal particles, seems to be subtle since results with less acidic catalyst supports such as γ-alumina show lower liquids and PD selectivity.

Collecting all arguments shows that the conversion of glycerol into mainly PD involves an acid catalyzed dehydration to hydroxyacetone, forming CO₂ and subsequent hydrogenation to PD (Scheme). Although details on the gas formation are still under study and the present note is not meant to divulge detailed kinetics, it is clear that the size of the metal particles is crucial at the start of the reaction sequences, as intrazeolitic Pt favors gas formation and decreased liquids and PD selectivity compared to extra-framework large Pt metal particles. The proposed mechanistic pathways on the optimally balanced catalyst (Pt/NaY) assume that initially formed CO₂ is at the origin of solution acidity and subsequently suitable zeolite acidity, catalyzing the dehydration of glycerol into hydroxyacetone. The hydrogenation of the latter preferably on metal particles external to the zeolite crystals seems to suggest the structure sensitive nature of the hydrogenation of hydroxyacetone into PD. Catalytic experiments suggest a kinetic network for major as well as minor kinetic pathways on the best system (Pt/NaY).

Significance

Sustainable production of chemicals is a relevant issue today. Provided glycerol is available at cheap price, it is a useful renewable for chemicals production, in particular when high added value is perceived. In situ producing “green” H₂ makes the process independent on fossil carbon.

References