

Improve the Reaction Efficiency in Synthesis 1,4-ButaneDiol (BDO) by Nano Copper Chromite Catalyst

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Abstract

The new coupling process of the dehydrogenation of 1,4-butanediol (BDO) and the hydrogenation of furfural (FFA) over a Nano copper chromite catalyst was carried out in a continuous fixed-bed reactor. The effects of the reaction conditions on the coupling process were investigated in detail. The results show that the coupling process has some advantages over the individual dehydrogenation and hydrogenation ones, such as optimal hydrogen utilization, good energy efficiency, improved yield and mild reaction condition.

Keywords

Nano Copper Chromite, 1,4-ButaneDiol, Presence of Hydrogen

1. Introduction

Table 1. 1,4-BDO properties.

Property	Value and specification
Appearance	Colorless and viscous liquid
Molecular weight	90.12 g/mole
Melting point	19°C
Boiling point	230°C
Vapor density	3.1 g/cm ³
Density	1.02 g/cm ³
Flash point	121°C
Water solution ability	Aqueous
Vapor pressure	0.014 hpa in 25°C
Self-burning point	402.5°C

1,4-Butanediol, colloquially known as BD, is the organic compound with the formula HOCH₂CH₂CH₂CH₂OH. It is a colorless viscous liquid. It is one of four stable isomers of butanediol. In its industrial synthesis, acetylene reacts with

two equivalents of formaldehyde to form 1,4-butanediol. This type of acetylene-based process is illustrative of what is known as "Repe chemistry", after German chemist Walter Repe. Hydrogenation of 1,4-butanediol gives 1,4butanediol. LyondellBasell manufactures 1,4-butanediol in a multi-step process without the use of acetylene. First, propylene oxide is converted to allyl alcohol. The allyl alcohol is then hydroformylated to 4-hydroxybutyraldehyde. Hydrogenation of this aldehyde yields 1,4butanediol. It is also manufactured on an industrial scale from maleic anhydride in the Davy process, which is first converted to the methyl maleate ester, then hydrogenated. Other routes are from butadiene, allyl acetate and succinic acid. A biological route to BDO has been commercialized that uses a genetically modified organism. The biosynthesis proceeds via 4-hydroxybutyrate. 1,4-Butanediol is used industrially as a solvent and in the manufacture of some types of plastics, elastic fibers and polyurethanes. In organic chemistry, 1,4-butanediol is used

for the synthesis of γ -butyrolactone (GBL). In the presence of phosphoric acid and high temperature, it dehydrates to the important solvent tetrahydrofuran. At about 200°C in the presence of soluble ruthenium catalysts, the Diol undergoes dehydrogenation to form butyrolactone. Physical and chemical properties of this compound showed in table 1.

2. 1,4-BDO Synthesis Methods

2.1. Synthesis by Acetone as Primary Material

3-liter two-neck round-bottomed flask fitted with a dropping funnel and two efficient reflux condensers in series into the other. 60 grams of clean dry sodium (the surface layer must be completely removed-see) are placed in the flask, and from the separator funnel protected by a drying tube a solution of 35 grams of diethyl succinate are added in 700 ml of absolute ethyl alcohol as rapidly as possible consistent with the reaction being under control. If reaction becomes too violent it may be necessary to immerse the flask momentarily in a cooling mixture. When the vigorous action has subsided, the mixture is warmed for 30-60 minutes in an oil bath at 130° C until all the sodium has reacted. The solution is cooled to room temperature and cautiously 25 ml of water are added. The reaction mixture is refluxed for a further 30 minutes in order to bring all the solid into solution and to hydrolyze any remaining ester. 270 ml of concentrated hydrochloric acid are added to the cold reaction mixture, which is cooled in ice, filtered the precipitated sodium chloride and treated the filtrate with 300 g of anhydrous potassium carbonate in order to remove remaining water and acid. The alcoholic solution is filtered through a large sintered glass funnel and extracted the solid twice with boiling alcohol. The alcohol is removed by evaporation from the combined solutions; towards the end of the distillation solid salts separates, which is treated with dry acetone, the mixture is filtered and distilled by evaporation in order to remove the acetone. The residue is distilled under diminished pressure collecting the fraction 1,4-butanediol of boiling at 133-135° C/18 mm. The yield of is 1,4-butanediol 13 grams. Alternatively, the following procedure for isolating the 1,4-butanediol may be used. The partly cooled mixture is diluted with 250 ml of water, then transferred to a distilling flask, and distilled from an oil bath until the temperature reaches 95° C. The hot residue is placed to an apparatus for continuous extraction with ether as the glycol is not very soluble in ether. Benzene may also be employed as the extraction solvent. When the extraction is complete the ether is removed by evaporation and after removal of the water and alcohol, the 1,4-butanediol is distilled under reduced pressure.

2.2. Synthesis by Aldehyde and Acetylene as Primary Material

Historically, acetylene-based production is the most embedded into BDO industry. BDO produced via Reppe

chemistry still accounts for about 40 percent of the global BDO capacity. Acetylene is reacted with formaldehyde to form butynediol (BYD) which then undergoes high-pressure hydrogenation to form BDO. The efficiency of the technology focuses on acetylene purification (via CaC_2 from coal) in conjunction with proprietary catalyst and reactor technology, followed by BDO refining steps. The produced BDO undergoes ring closing chemistry to form THF. This method is industrial synthesis method of 1,4-BDO that acts in 3 steps [1]. In first step, Formaldehyde and Acetylene act together in presence of on organic catalyzer and synthesis 1,4-BDO. Next step, Acetylene-Diol reduce in presence of a reducer catalyzer like H_2/Pd and convert to 1,4-BDO. Finally, the material is separated by distillation column.

2.3. Synthesis by 4-carbon Di-Carboxylic Acid or Its Derivations as Primary Material

By this method, catalytic hydrogenation of 4-carbon Di-Carboxylic acid act in presence of Cu and Cr catalysts in gas phase that leads to synthesis of GBL. GBL converts to BDO in presence of Cu-Chromite catalyzer [2]. GBL vapor and water vapor and Hydrogen gas transition above the Cu-Zn catalyzer cause increasing efficiency.

2.4. Synthesis by Di-Hydro Furan as Primary Material

By this method, 2,3- Di-Hydro Furan hydrogenate catalytic in presence of water and Hydrogen in 20-300°C and pressure of 1-300 bar in neutral or acidic conditions and mixture of 4-Hydroxi Butyr Aldehyde and Isomer of 2-Hydroxi Tetra Hydro Furan synthesized [3]. This productions in first step, convert to 1,4-BDO in presence of Hydrogen and Rhodium, Ruthenium and cobalt catalyzers with Phosphine or phosphide ligands.

2.5. Synthesis by Maleic Anhydride as Primary Material

Since its initial development in the 1990s, Davy has continued to simplify its maleic anhydride (MAN) esterification process and subsequent hydrogenation process, reducing complexity, equipment requirement, and overall capital costs. Notable improvements are its transition into di-esterification of MAN with methanol to form DMM, followed by hydrogenation of DMM into DMS and through to BDO. Additionally, DPT has integrated isolation methods for key derivatives GBL and THF. These options allow for chemical producers to convert n-butane to three key derivative products that are core to the plastic, rubber, and fiber industries. By this method, a solution of Maleic anhydride converts to 1,4-BDO in presence of Mono-Hydric Aliphatic alcohol and catalyzer [4-11]. This process is a single step process and temperature is 15-60°C.

2.6. Synthes Methods Comparison

In synthesis method by Aldehyde and Acetylene, primary

materials are available. Formaldehyde has environmental problems due to toxicity. Because of process complexity, bench and pilot synthesis scales aren't suitable, but is able to industrial scale synthesis. By 4-carbon Di-Carboxylic acid synthesis, primary materials are available. Because of using metallic oxides catalyzers, this method is complex and for its high condition of temperature and pressure isn't economical efficiency. Although this method has no environmental problems but because of mentioned problems, it isn't an appropriate method. In synthesis by Di-Hydro Furan, used catalyzers are expensive and isn't economical efficiency. The synthesis efficiency is low and it isn't need to separate the main product from intermediate products. Work conditions of temperature and pressure are relatively high but hasn't much environmental problems. So this method isn't an appropriate

method. Method of synthesis BDO by presence of Hydrogen method, primary materials aren't available. The efficiency is low and using Octa Carbonyl Di-Cobalt isn't economical. The process of electrical reduction has complexity and isn't compatible with industrial structures. According to that didn't reported any environmental problems, but this method isn't appropriate method. Among presented methods of synthesis of BDO, method of Maleic anhydride using, is a relatively good method because of availability of primary materials, single step process, suitable reaction conditions and no environmental problems. As the table 2 shows each of mentioned methods has advantages and disadvantages in synthesis of BDO: In this way, we chose method presence of Hydrogen for research.

Table 2. BDO synthesis methods compare.

Synthesis method	Aldehyde and Acetylene	4-carbon DiCarboxylic acid	2,3-Di-HydroFuran	Maleic Anhydride	presence of Hydrogen
Primary materials availability	Available	Available	Not available	Available	Not available
Efficiency	Relatively high	Relatively low	Relatively low	High	Low
Process complexity	Complex	Complex	Complex	Simple	Complex
Environmental problems	Yes	No	No	No	No
Economical efficiency	Yes	No	No	Yes	No
Increasing production scale	No	No	No	Yes	No

3. Empimental Section

The used equipment for synthesis BDO, preparing, sample producing, casting, cutting and mechanical tests are below: Steel reactor, autoclave 500ml for catalytic reduction reaction and FT-IR (Nicolet 860) device for infrared tests, FT-NMR

device Bruker, 500MHZ-DPX3300 model with DMSO solvent and Tetra-methyl silane (TMS) as standard case, Digital melting point IA 8103 device for measuring melting point also used Thin Layer Chromatography (TLC) for studying reaction progress.

4. Synthesis 1, 4-BDO by Nano Copper Chromite Catalyst

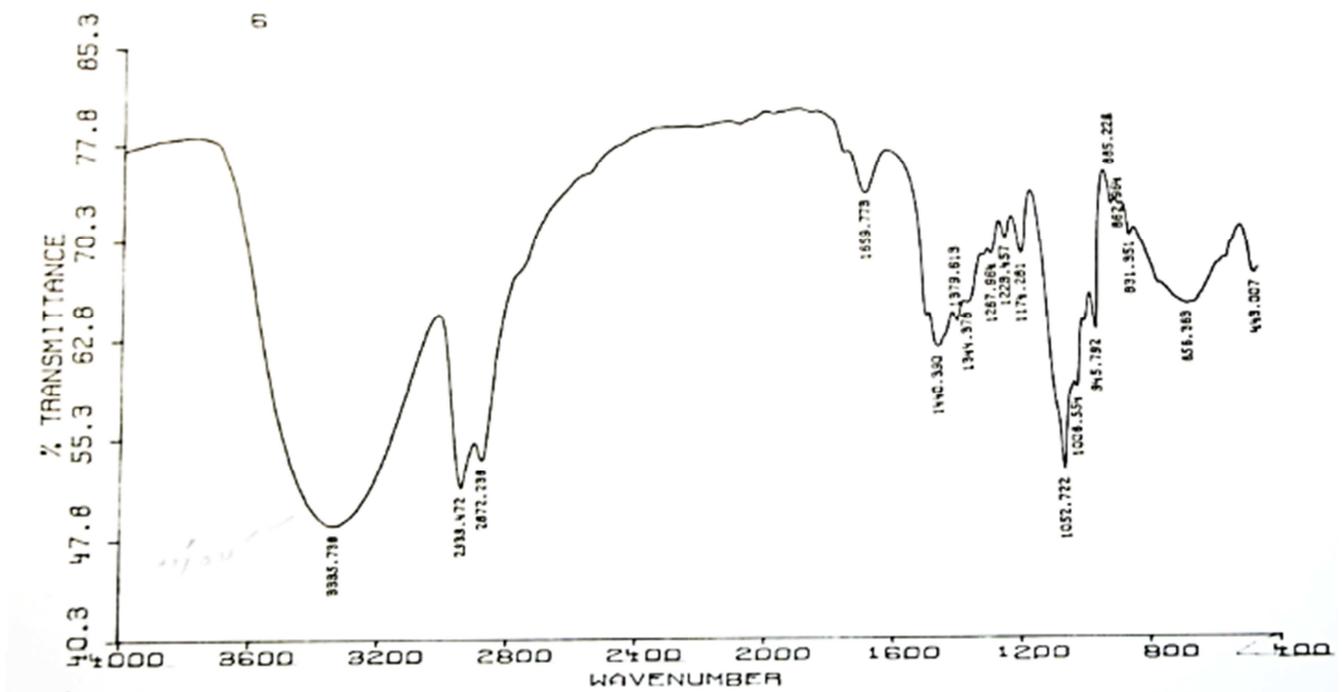


Figure 1. FT-IR test results of 1,4-BDO.

First, the Nano-catalyst was synthesized by self-combustion sol-gel citrate method [12]. After more, a solution of Maleic anhydride converts to 1,4-BDO in presence of Hydrogen and Mono Hydric Alcohol. First, prepare the catalyzer in 900 psig and 120°C in presence of Hydrogen then reaction acts in 55°C. The FT-IR and Hydrogen spectrum results are below. As in figure 1 shows, totally there are three peaks in compound. The first one is for two of Hydrogen of OH groups that has 4.5 ppm peak in H-NMR test. The second peak is for the type of 4 Hydrogen groups that relates to Methyl connected groups and has 1.4 ppm peak. Because of OH group there is a wide peak in FT-IR spectrum that is higher than 3000 and about 3300-3400 cm^{-1} . Also because of first type of alcohol, there is a peak in 1050 cm^{-1} area. Results shows that using catalyzer cause increasing efficiency of 1,4-BDO synthesis reactions.

5. Conclusion

In summary the results shows that when use the Nano Cu-Chromite catalyzer a high impact on efficiency has been reported, the and efficiency increases significantly. This reaction acts by Nano Cu-Chromite catalyzer macro scale and the efficiency was 70-75 percentages but by using nano scale catalyzer the efficiency is about 100%.

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