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HYDROGENATION OF 1,4-BUTYNE-2-DIOL TO 1,4-BUTANEDIOL

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This invention relates to the catalytic hydrogenation of 1,4-butyne-2-diol, hereinafter referred to as butynediol, to 1,4-butanediol, hereinafter referred to as butanediol.

The hydrogenation of butynediol to butanediol in the presence of a number of different catalysts and by a number of different procedures is known. However, such previously proposed processes have been deficient for a number of reasons, including the necessity for using specially prepared or poisoned catalysts, high pressures, careful control to avoid production of undesirable by-products and/or the like. A nickel catalyst has been successfully employed in such a process, but this process likewise requires the use of very high pressures of the order of 200 or more atmospheres.

It is an object of this invention to provide a hydrogenation process for the reduction of butynediol to butanediol which is not subject to the above disadvantages. Another object of this invention is the provision of a process for the hydrogenation of butynediol to butanediol which may be carried out at relatively low temperatures and pressures. Another object of this invention is the provision of a process for the hydrogenation of butynediol to butanediol in the presence of a nickel catalyst at relatively low temperatures and pressures without substantial detriment to the yields of the desired product and/or without the simultaneous production of any substantial amounts of undesirable by-products which would reduce the quality and yield of product desired. Other objects and advantages will appear as the description proceeds.

The attainment of the above objects is made possible by the instant inventive process for the catalytic hydrogenation of butynediol to butanediol comprising treating a solution of butynediol with hydrogen at a temperature of about 15 to 100° C. and a pressure of about 0 to 40 atmospheres gauge in the presence of a nickel catalyst carrying about 3 to 15% of copper by weight of the nickel catalyst. It has been found that the concurrent use of copper in the above defined process has little or no effect on the activity of the nickel catalyst for hydrogenation but acts to suppress isomerization during the process which would tend to produce by-products having a detrimental effect upon the quality and yield of the desired butanediol. Further, the use of copper in this process enables the attainment of large savings in cost of operation and equipment because of the relatively low pressures which may be employed. The catalyst maintains its activity much longer, possibly because of the lowering of the formation of by-products, including gamma-hydroxybutyraldehyde, tetrahydrofuran, dihydrofuran, propionaldehyde, and the like, and the poisoning produced thereby, and may accordingly be reused repeatedly.

In carrying out the process of this invention, the butynediol is maintained in liquid condition at a pH of no more than about 7, preferably in solution in an inert solvent such as ethyl alcohol or other alcohols, dioxane, or the like, but preferably in an aqueous solution. Con-

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centrated solutions are preferred, an aqueous solution having a concentration of at least about 20%, and preferably 35 to 40% having been found highly advantageous and convenient. Such solutions are available commercially at a pH of about 2.5 to 6. If desired, undiluted liquid butynediol may be used.

The nickel catalyst employed in the process of this invention is preferably maintained in the liquid butynediol reaction medium in finely divided form. A Raney-type nickel catalyst (such catalysts are described in U.S. Patent No. 1,638,190) is preferred as yielding optimum results. This type of catalyst is readily prepared by treating an aluminum-nickel alloy with caustic soda to dissolve out the aluminum and leave the nickel in a highly divided and particularly effective form. The amount of nickel catalyst employed will generally range from about 0.1 to 10%, and preferably from about 0.5 to 3% by weight of the butynediol, but such amount is not critical since the catalyst is not deactivated during the hydrogenation and may be reused. For a given amount of butynediol to be hydrogenated, the rate of hydrogenation will vary directly with the amount of catalyst employed.

In accordance with the instant process, the desired improved results and advantages are obtained when the butynediol-nickel catalyst system also contains dispersed thereon about 3 to 15% of copper by weight of the nickel catalyst, preferably as deposited from a soluble or dispersible copper compound. When an aqueous solution of butynediol is employed, a water soluble copper compound is preferably added thereto, particularly the copper salts of strong acids such as copper sulfate, copper chloride, and copper nitrate, and the copper salts of weak acids such as copper cyanide, copper formate, copper acetate and copper carbonate. Copper oxide may also be used. Some of these compounds are also soluble in organic solvents. The particular copper compound employed will of course be dependent upon the liquid reaction medium. The nickel replaces the copper from the solution and any residual soluble copper is reduced during the hydrogenation. The precipitated copper is dispersed or coated on the nickel catalyst.

The hydrogenation of the butynediol in the reaction medium is carried out by maintaining an atmosphere of hydrogen over the surface of the reaction medium, contact therewith being facilitated by agitation as by rocking or shaking the reaction vessel, or by stirring the reaction medium with a high speed propeller or the like. Within the defined temperature range, use of a lower temperature yields a product of higher quality, but the reaction rate is lower. The optimum temperature range is about 40 to 60° C. At higher temperatures, reduction is incomplete and considerable butenediol is produced, as disclosed and claimed in my copending application Serial No. 704,240 filed on even date herewith, unless pressures of more than 4 atmospheres gauge are employed. Apparently, at temperatures of over 60° C. under the conditions of the hydrogenation, some substance present in the reaction medium acts to prevent complete reduction to the butanediol stage unless the pressure is increased as above noted. Such substance does not, however, poison the catalyst which may be reused repeatedly. Completion of the desired hydrogenation is indicated when absorption of hydrogen ceases, contact with the hydrogen being preferably continued for a further period to insure completion of this reaction.

The examples in the following table in which parts are by weight unless otherwise indicated are illustrative of the instant invention and are not to be regarded as limitative. In each of the examples, a rocking autoclave containing 3.0 moles of technical 35% aqueous butynediol and 6.0 g. (solids) of Raney-type nickel in the form of a 50% aqueous paste is held at 40° C. while

maintaining therein the indicated hydrogen pressure in pounds per square inch gauge (p.s.i.g.) for three hours after the indicated time when hydrogen absorption ceased. In each case, the product is filtered from the catalyst, fractionally distilled, and the yield of the desired butanediol, and its properties, determined. In Examples 2, 4 and 6, 2.0 g. of copper acetate is added to the solution prior to hydrogenation.

Table

Example	Pressure	Time, Hours	Yield, Percent	S.P., ° C.	N _D ²⁵
1. (No Cu)-----	75	22	78.5	10.8	1.4466
2. (Cu)-----	75	20	83	13.3	1.4460
3. (No Cu)-----	150	7.5	84.5	11.7	1.4464
4. (Cu)-----	150	8	88	16.4	1.4458
5. (No Cu)-----	300	4.5	87	12.6	1.4461
6. (Cu)-----	300	4.5	89	16.9	1.4451

In the above table, the refractive index of each product is given in the right-hand column, and the solidification point in the column adjacent thereto. Pure butanediol has a solidification point of about 20.9° C. and a refractive index of about 1.4446. The results shown in the table indicate that Examples 2, 4 and 6 carried out in the presence of copper in accordance with the instant invention, enable the attainment of improved yields of purer product as compared with comparative Examples 1, 3 and 5 in which no copper was used.

This invention has been disclosed with respect to certain preferred embodiments, and there will become obvious to persons skilled in the art various modifications, equivalents or variations thereof which are intended to be included within the spirit and scope of this invention.

I claim:

1. A process for the catalytic hydrogenation of 1,4-butyne-1,3-diol to 1,4-butanediol comprising treating 1,4-butyne-1,3-diol in liquid form with hydrogen at a pH of no more than about 7, a temperature of about 15 to 100° C. and a pressure of about 0 to 40 atmospheres gauge in the presence of a nickel catalyst carrying about 3 to 15% of copper by weight of the nickel catalyst, the pressure being more than 4 atmospheres gauge at temperatures of 60 to 100° C.

2. A process as defined in claim 1 wherein the nickel catalyst is a Raney-type nickel catalyst.

3. A process as defined in claim 1 wherein the copper is derived from copper acetate.

4. A process for the catalytic hydrogenation of 1,4-butyne-1,3-diol to 1,4-butanediol comprising treating an aqueous solution of 1,4-butyne-1,3-diol with hydrogen at a pH of no more than about 7, a temperature of about 15 to 100° C. and a pressure of about 0 to 40 atmospheres gauge in the presence of a nickel catalyst carrying about 3 to 15% of copper by weight of the nickel catalyst, the pressure being more than 4 atmospheres gauge at temperatures of 60 to 100° C.

5. A process as defined in claim 4 wherein the nickel catalyst is a Raney-type nickel catalyst.

6. A process for the catalytic hydrogenation of 1,4-butyne-1,3-diol to 1,4-butanediol comprising treating a solution containing 1,4-butyne-1,3-diol, a nickel catalyst and about 3 to 15% of copper, in the form of a water dispersible copper compound by weight of the nickel catalyst, with hydrogen at a pH of no more than about 7, a temperature of about 15 to 100° C. and a pressure of about 0 to 40 atmospheres gauge, the pressure being more than 4 atmospheres gauge at temperatures of 60 to 100° C.

7. A process as defined in claim 6 wherein the nickel catalyst is a Raney-type nickel catalyst.

8. A process as defined in claim 6 wherein the copper compound is copper acetate.

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