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HYDROGENATION OF ALKYNOLS AND ALKYNEDIOLS

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ABSTRACT OF THE DISCLOSURE

Hydrogenation of alkynols and alkynediols to the corresponding saturated alcohols at elevated temperature and at superatmospheric pressure in the presence of catalysts which contain nickel and/or cobalt and additions of copper and manganese and/or chromium in the ratio of nickel:cobalt:copper:manganese/chromium of 40-89:10-40:1-20% by weight with reference to the metal content of the catalysts, and also a pyroacid or polyacid in free form and/or in the form of at least one salt of the said metals. The products are suitable as solvents or as starting materials for high polymers.

The invention relates to a process for the hydrogenation of alkynols and alkynediols to the corresponding saturated alcohols.

It is known from U.S. Patents Nos. 2,863,929, 3,177,258 and 2,992,278 that butynediol can be hydrogenated in the presence of noble metal catalysts, such as palladium and ruthenium. Noble metals are however expensive in large scale operation. Moreover British Patents Nos. 799,206 and 918,273, U.S. Patents Nos. 2,768,214, 2,908,712, 3,184,513, 2,967,893, 2,335,798 and 2,319,707 and German Patent No. 897,553 have described that nickel and cobalt, if desired with additions of copper, chromium and/or manganese are suitable catalysts for the hydrogenation of alkynediols. The saturated alcohols prepared by the said methods do not satisfy requirements as regards purity. The rapid decline in the activity of the catalyst means that the hydrogenation proceeds only incompletely so that compounds which have been only partly hydrogenated or not at all, or other impurities, remain in the product and can only be removed by expensive distillation. Moreover quite considerable amounts of butanol are formed in the hydrogenation of butynediol.

It is an object of the invention to provide an improved process by which saturated alcohols are obtained in high purity. Another object of the invention is to provide a process in which the catalysts used have a long life while retaining a constant activity. A further object of the invention is to provide a process in which higher throughputs than hitherto are achieved in the same size of apparatus owing to the high activity of the catalyst. Yet another object of the invention is to provide a process in which the hydrogenation of butynediol takes place with the formation of particularly small amounts of butanol.

These and other objects are achieved in accordance with this invention by hydrogenation of alkynols and alkynediols to the corresponding saturated alcohols at elevated temperature and superatmospheric pressure in the presence of catalysts which contain nickel and/or cobalt and additions of copper and manganese and/or chromium in the ratio of nickel:cobalt:copper-manganese/chromium of 40-89:10-40:1-20% by weight (based on the metal content of the catalyst) and a pyroacid or

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polyacid in free form and/or in the form of at least one salt of the said metals.

The preferred starting materials are aliphatic alkynols or alkynediols having three to twelve, particularly three to six, carbon atoms. The triple bond may be present once or more than once, for example twice, in the molecule. Starting materials are also suitable which have substituents which are inert under the reaction conditions, such as alkyl radicals having one to four carbon atoms, if desired attached by ether bridging groups. The following may be used, for example, for the hydrogenation:- propargyl alcohol, butyne - (2) - diol - (1,4), hexadiyne - (2,4) - diol - (1,6), 3,6 - dimethyloctyne - (4) - diol - (3,6), hexyne - (3) - diol - (2,5). The process has particular importance for the hydrogenation of butyne - (2) - diol - (1,4) and hexadiyne - (2,4) - diol - (1,6).

Hydrogenation is carried out in general at temperatures of 20° to 180° C., preferably at temperatures of 50° to 120° C. It is advantageous to use pressures of 0 to 500 atmospheres gauge, particularly 50 to 450 atmospheres gauge, preferably 200 to 400 atmospheres gauge.

Hydrogenation may be carried out in the presence of inert media, such as water or alcohols, for example ethanol or butanol, as well as cyclic ethers, such as tetrahydrofuran. It is advantageous to use for the hydrogenation the aqueous solutions in which the alkynols and alkynediols have been obtained, together with the hydrogenated reaction product.

The catalysts contain nickel and/or cobalt and an addition of copper and manganese and/or chromium in the ratio cobalt/nickel:copper:manganese/chromium of 40-89:10-40:1-20% by weight, particularly 55-84:15-35:1-10% by weight, based on the metal content of the catalysts. The catalysts also contain a pyroacid or polyacid in the form of the free acid and/or in the form of at least one salt of the said metals. In the production of the catalysts it is advantageous to start from acids which change upon being heated into their pyro or poly form, such as phosphoric acid, boric acid, molybdic acid or tungstic acid. It is particularly preferred to use phosphoric acid. The acids or their salts are advantageously used in an amount of .5 to 15% by weight based on the metal content of the catalysts. Particularly good results are obtained with contents of 1 to 10% by weight. All the percentages refer to the contents of the individual components determined analytically in the finished catalysts, the metals being given as such and the pyroacids or polyacids or their salts being given as anhydrides, i.e. independently of the actual state of combination. The catalysts may be used unsupported. In this case the individual constituents of the catalyst are mixed in the form of compounds which can be reduced with hydrogen at elevated temperatures, such as oxides, hydroxides, oxalates, ammoniates or formates, with the addition of the stated amounts of the said acids which change into their pyro or poly form when heated, heated preferably to 300° to 700° C. and then reduced with hydrogen at elevated temperature, advantageously at 200° to 400° C. In a preferred method for the production of the catalysts, the metals and acids are precipitated together from a solution with alkali, such as sodium carbonate or sodium hydroxide, and the precipitate is heated, for example in a muffle furnace, at about 300° to 700° C. The mixture is then powdered and pressed into tablets or pellets and then reduced with hydrogen at elevated temperature. It is also possible to apply the metal salts and the acids to a carrier, such as fuller's earth, silicic acid, silica gel, aluminum oxide or silicates, to heat them, for example in a muffle furnace, to about 300° to 700° C. and then to reduce them with hydrogen as described. It has proved to be particularly advantageous to effect pre-

cipitation of the metal components and the acids onto a powdered carrier, or to effect coprecipitation with the carrier from a solution, for example with sodium carbonate, to heat the precipitate at about 300° to 700° C. for example in a muffle furnace and then to reduce it with hydrogen as described.

The process according to the invention may for example be carried out by forcing hydrogen to the point of saturation in a high pressure vessel into the alkynols or alkynediols to be hydrogenated in the presence of a catalyst of the said composition at the said temperature and pressure conditions. On a commercial scale the process is advantageously carried out continuously by charging a vertical high pressure tube with the catalyst, metering in alkynol or alkynediol at the top and supplying hydrogen countercurrent or cocurrent under the stated conditions at the same time. In a particularly advantageous continuous method, the alkynols or alkynediols are fed into the top of the high pressure tube with about .5 to 10 times the amount, preferably once to five times the amount, of hydrogenated product, with reference to the alkynols or alkynediols used. The crude alcohols are fractionally distilled to purify them. They are distinguished by a particularly low iodine number.

Saturated alcohols prepared by the process according to this invention are suitable as solvents and for the production of high polymers (cf. J. Am. Chem. Soc., 72, 1674 (1950)).

The invention will be further described in the following examples in which parts are by weight unless stated otherwise. Parts by weight bear the same relation to parts by volume as the kilogram to the liter.

Example 1

A solution of 3500 parts of cobalt nitrate having six molecules of water of crystallization ($6\text{H}_2\text{O}$), 769 parts of copper nitrate ($3\text{H}_2\text{O}$), 262 parts of manganese nitrate ($6\text{H}_2\text{O}$) and 47 parts of 85% by weight phosphoric acid in 8000 parts by volume of water is allowed to flow at 40° C. while stirring into a solution of 1700 parts of anhydrous sodium carbonate and 8000 parts by volume of water. The precipitate is suction filtered and washed with water until as free as possible from alkali. The washed filter cake is dried and then heated to 300° C. The mixture is powdered and shaped into pellets having a diameter of 4 mm. The pellets are charged into a vertical high pressure tube having a capacity of 6360 parts by volume and reduced with hydrogen at 300° C. The finished catalyst contains cobalt, copper and manganese in the ratio by weight 71:20:5 and 2.9% by weight of phosphorus pentoxide with reference to cobalt, copper and manganese.

300 parts by volume of a 31.8% by weight aqueous solution of butyne-(2)-diol-(1,4) and 600 parts by volume of the butanediol solution discharged from the high pressure tube are metered in per hour at 55° C. to the top of the high pressure tube which is filled with catalyst and under a pressure of 300 atmospheres gauge of hydrogen. The hydrogen is recycled through a heat exchanger to remove heat. The butanediol solution obtained is then fractionally distilled. 98.9 parts per hour of butanediol-(1,4) is obtained (98.8% of the theory). The low proportion of .25 part (.25%) of butanol and of .5 part (.5% of the theory) of residue are particularly remarkable. The iodine number of the butanediol is .1.

Example 2

A solution of 864 parts of cobalt nitrate ($6\text{H}_2\text{O}$), 227 parts of copper nitrate ($3\text{H}_2\text{O}$), 46.6 parts of manganese nitrate ($6\text{H}_2\text{O}$) and 7 parts of 85% by weight phosphoric acid in 4000 parts by volume of water is allowed to flow at 40° C. while stirring well into a solution of 460 parts of anhydrous sodium carbonate in which 752 parts of aluminum oxide powder is suspended. The precipitate is filtered off and further treated according to Example 1.

The finished catalyst contains cobalt, copper and manganese in the ratio by weight 17.5:6:7 and 1.8% by weight of phosphorus pentoxide with reference to cobalt, copper and manganese.

An aqueous butyne-(2)-diol-(1,4) solution is hydrogenated with the reduced catalyst under the conditions described in Example 1. 97.5 parts per hour of butanediol-(1,4) is obtained (97% of the theory). Moreover .5 part of butanol (.5% of the theory) and 1.71 parts of residue (1.7% of the theory) are obtained. The iodine number of the butanediol is .15.

Example 3

A solution of 5640 parts of aluminum nitrate, 864 parts of cobalt nitrate ($6\text{H}_2\text{O}$), 199 parts of copper nitrate ($3\text{H}_2\text{O}$), 36.5 parts of manganese nitrate ($6\text{H}_2\text{O}$) and 7.1 parts of 85% by weight phosphoric acid in 20,000 parts by volume of water is allowed to flow at 50° C. with good stirring into a solution of 3150 parts of anhydrous sodium carbonate in 15,000 parts by volume of water. The precipitate is worked up as described in Example 1. The finished catalyst contains cobalt, copper and manganese in the weight ratio 17:5:7 and 1.92% by weight of phosphorus pentoxide, with reference to cobalt, copper and manganese. An aqueous solution of butyne-(2)-diol-(1,4) is hydrogenated with the reduced catalyst under the same conditions as described in Example 1. 98.7 parts per hour of butanediol-(1,4) (98.1% of the theory) and also .5 part of butanol (.5%) and 1.3 parts of residue (1.3%). The iodine number of the pure butanediol-(1,4) is .15.

Example 4

Hydrogen is forced at 60° C. into a high pressure tube having a capacity of 1000 parts by volume which is rotating about its longitudinal axis and which has been charged with 50 parts of the catalyst described in Example 1 and 450 parts of propargyl alcohol, until the pressure is 300 atmospheres gauge. Absorption of hydrogen is ended after one hour. The catalyst is filtered off after it has cooled. The filtrate contains 99.8% by weight of n-propanol according to gas chromatographic analysis.

Example 5

A solution of 493 parts of nickel nitrate ($6\text{H}_2\text{O}$), 395 parts of cobalt nitrate ($6\text{H}_2\text{O}$), 227 parts of copper nitrate ($3\text{H}_2\text{O}$), 37 parts of manganese nitrate ($6\text{H}_2\text{O}$) and 6 parts of phosphoric acid calculated at 100% in 10,000 parts by volume of water is allowed to flow at 40° C. with good stirring into a solution of 437 parts of anhydrous sodium carbonate in 10,000 parts by volume of water in which 747 parts of precipitated silicic acids has been suspended. The precipitate is filtered off and further treated according to Example 1. The finished catalyst contains nickel, cobalt, copper and manganese in the weight ratio 10:8:6:7 and 1.75% by weight of phosphorus pentoxide with reference to nickel, cobalt, copper and manganese.

An aqueous solution of butyne-(2)-diol-(1,4) is hydrogenated with the reduced catalyst under the conditions described in Example 1. 97.4 parts of butanediol-(1,4) is obtained per hour (97.2% of the theory). .9 part of butanol (.9% of the theory) and 1.6 parts of residue (1.6% of the theory) are also obtained. The increase in residue as compared with the butanediol residue is .7%. The iodine number of the butanediol is .12.

Example 6

A solution of 888 parts of nickel nitrate ($6\text{H}_2\text{O}$), 227 parts of copper nitrate ($3\text{H}_2\text{O}$), 47 parts of manganese nitrate ($6\text{H}_2\text{O}$) and 9 parts of phosphoric acid calculated at 100% in 10,000 parts by volume of water is allowed to flow at 50° C. with good stirring into a solution of 440 parts of anhydrous sodium carbonate in 10,000 parts

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of water in which 742 parts of aluminum hydroxide is suspended.

The residue is worked up as described in Example 1. The finished catalyst contains nickel, copper and manganese in the weight ratio 18:6:9 and 2.6% by weight of phosphorous pentoxide with reference to nickel, copper and manganese.

An aqueous solution of butyne-(2)-diol-(1,4) is hydrogenated with the reduced catalyst under the conditions described in Example 1. 97.1 parts of butanediol-(1,4) is obtained per hour (96.5% of the theory). 1.2 parts of butanol (1.2% of the theory) and 1.5 parts of residue (1.5% of the theory) are also obtained. The increase in residue is .7%. The iodine number of the butane diol is .11.

Similar results are obtained by replacing some or all of the manganese by chromium.

We claim:

1. An improved process for the hydrogenation of alkynols and alkynediols having three to twelve carbon atoms to the corresponding saturated alcohols at temperatures of 20° to 180° C. and pressures of hydrogen of 0 to 500 atmospheres gauge in the presence of an inert solvent and a catalyst in which the improvement comprises using in said process a catalyst which contains, exclusive of any support, 40 to 89% by weight of a member selected from the group consisting of nickel, cobalt and mixtures thereof, 10 to 40% by weight of copper, 1 to 20% by weight of manganese and 0.5 to 15% by weight of pyrophosphoric acid or polyphosphoric acid, calculated as phosphorous pentoxide, said pyrophosphoric acid or polyphosphoric acid being in the free form or in the form of at least one salt of the said metals, the aforesaid percentages being based on the metal content of said catalyst.

2. A process as claimed in claim 1 wherein alkynols or alkynediols having three to six carbon atoms are used.

3. A process as claimed in claim 1 wherein butyne-(2)-diol-(1,4) is used.

4. A process as claimed in claim 1 carried out at a temperature of 50° to 120° C.

5. A process as claimed in claim 1 wherein a pressure of 50 to 450 atmospheres gauge is used.

6. A process as claimed in claim 1 wherein the hydrogenated reaction product is used as solvent.

7. A process as claimed in claim 1 wherein the alkynol or alkynediol is subjected to hydrogenation together with .5 to 10 times the amount of hydrogenated reaction product.

8. A process as claimed in claim 1 wherein a catalyst fixed on a carrier is used.

9. A process as claimed in claim 1, wherein the catalyst contains, exclusive of any support, 1 to 10% by weight of a pyrophosphoric or polyphosphoric acid calculated as phosphorous pentoxide, said percent being based on the metal content of said catalyst.

10. A process as claimed in claim 1, wherein a catalyst is used which has been prepared by coprecipitation of the metal components and phosphoric acid.

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