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HYDROGENATION OF ESTERS

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No Drawing. Application March 29, 1954,
Serial No. 419,575

7 Claims. (Cl. 260—638)

This invention relates to the production of lower aliphatic alcohols by the hydrogenation of esters under the influence of a catalyst and more particularly this invention is directed to a process for the production of lower aliphatic monohydric alcohols from esters embodying the same by the hydrogenation of these esters in the presence of a catalyst consisting of copper oxide promoted with chromium oxide and containing from 1 to 5 parts of chromium per 100 parts of copper.

One of the significant features of this invention is that now a process is available commercially which will permit the production of ethanol and methanol in substantial yield by the vapor phase hydrogenation of methyl acetate at a temperature above its critical temperature and at an elevated pressure in the presence of a catalyst consisting of copper oxide promoted with chromium oxide and containing from 1 to 5 parts of chromium per 100 parts of copper.

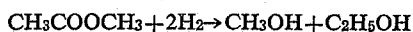
Heretofore, ethanol and methanol have not been produced by the reaction of hydrogen with methyl acetate, but it is known that alcohols of higher molecular weight may be produced by the catalytic hydrogenation of esters of aliphatic carboxylic acids, utilizing various catalysts such as, for example, copper oxide preferably promoted with an oxide of an alkali or alkaline earth metal; chromium oxide alone or in conjunction with tungstates, vanadates or molybdates; cobalt salts of metal acids deposited on a carrier; reduced copper oxide alone or in conjunction with oxides of zinc, magnesium, manganese and the like. All of these heretofore known processes are essentially liquid phase operations and although vapor phase operations have been proposed they have not been efficient and the yields of products are low.

While the processes of hydrogenating esters of aliphatic monocarboxylic acids are thoroughly discussed in the literature, the particular processes for hydrogenating methyl acetate to ethanol and methanol are few in number. The reason appears to be that methyl acetate and methanol are subject to gaseous decomposition during the hydrogenation processes utilized by the prior art. Thus, no suitable commercial processes exist for the conversion of methyl acetate to ethanol and methanol.

Therefore, it is one of the purposes of this invention to provide an essentially vapor phase process for the conversion of methyl acetate to ethanol and methanol which is highly efficient and results in substantial yields of products.

The process of this invention, however, in its broader aspects comprises the reaction of lower aliphatic esters in the presence of hydrogen at an elevated temperature and pressure in the presence of a catalyst consisting of copper oxide promoted with chromium oxide and containing from 1 to 5 parts of chromium per 100 parts of copper.

The reaction whereby the alcohols are produced in accordance with this invention may be represented, in the case of methyl acetate, by the following equation:



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Theoretically, the reaction calls for two mols of hydrogen per mol of ester but from a practical standpoint the ester is charged to the reaction vessel and reacted in a large excess of hydrogen.

The lower aliphatic esters which may be employed in the process of this invention can be esters such as, methyl acetate, ethyl acetate, methyl and ethyl propionate, methyl and ethyl butyrate and the like.

The hydrogenolysis conditions which may be advantageously employed in the process of this invention are similar to those conditions of hydrogenation which are generally employed in established hydrogenation techniques and are widely known as involving the use of elevated temperatures and pressures.

More specifically, though, it is preferred to employ an elevated temperature which is in the range of 250° C. to 400° C.

Pressures above 5,000 pounds per square inch are employed, excellent results being obtained when pressures in the range of 10,000–15,000 pounds per square inch are utilized.

The catalyst utilized in the process of this invention is prepared by the admixture of aqueous solutions of copper nitrate and chromium acetate. These solutions may be used to impregnate a catalyst support whereupon it is then roasted to produce a finished catalyst containing from 1 to 5 parts of chromium per 100 parts of copper.

A detailed example of the preparation of the catalyst in a preferred form involves the addition of approximately 6.6 parts by weight of copper scrap over a three hour period to 100 parts by weight of a 34 percent aqueous nitric acid solution maintained at a temperature of 90° C. When the acidity of the resulting copper nitrate solution is below 20 percent, calculated as nitric acid, 0.45 part of chromium is added as a concentrated aqueous chromium acetate solution. Then 6.5 additional parts of copper scrap are added over a period of three hours. The solution temperature is maintained at 90° C. by cooling or heating as required during all additions and until the acidity falls below 2.0 percent. The copper-chrome solution is then concentrated by evaporation until a specific gravity of 1.70–1.75 is obtained.

Preferably, a catalyst support should be employed in which case a suitable porous basket containing 0.375 x 0.261 mesh Filtros is immersed for 15 minutes in the impregnating solution having a specific gravity of 1.70–1.75 at the boiling temperature. After dipping and drainage the impregnated Filtros is roasted in a stream of air for a period of two hours at 350° C.

The catalyst is then dipped and roasted until the copper content is 12 percent and the chromium content is 0.3 to 0.4 percent, giving a weight ratio of 2.5–3.5 parts of chromium per 100 parts of copper.

The amount of catalyst necessary to promote the hydrogenation of methyl acetate is not a critical feature of this invention. An amount of catalyst sufficient to promote the reaction is all that is necessary. For batchwise reactions, however, a preferred range of catalyst concentration based on copper oxide is an amount equivalent to 1 to 5 percent, by weight, of the ester charged to the reaction vessel. The catalyst may or may not be supported by an inert carrier and may be charged in a loose form to the reaction vessel or suspended in a porous basket within the reaction vessel. For continuous reactions the amount of catalyst required depends upon the desired conversion and production rate, the supported catalyst being heated within a high pressure reactor and the vaporized lower aliphatic esters being passed together with hydrogen through the catalyst bed.

In carrying out the process of this invention, a rocker-type reaction vessel similar to those used in established techniques for laboratory hydrogenations can be utilized

although, as indicated above, the process can be operated in a continuous or semi-continuous manner. Methyl acetate, or the other lower aliphatic esters, may be hydrogenated in solution with one of the expected alcohols or an inert diluent by passing the reactants over a supported catalyst in the vapor phase.

In batchwise experiments the reaction vessel is charged with liquid and solid components and hydrogen is introduced at approximately 500 pounds per square inch pressure and expelled three times to purge the system completely. Hydrogen is then added to the reaction vessel to a pressure calculated to give the desired reaction pressure and the reaction vessel is heated to the desired operating temperature, the reaction system being maintained at the desired operating pressure. When the reaction conditions have been maintained for a sufficient period of time, the heating is discontinued and the reaction vessel and its contents cooled. The products are then discharged from the reaction vessel and recovered by any suitable means, such as for example, by fractional distillation.

The following examples will serve to illustrate the practice of the invention:

Example I

Methyl acetate, as an 82 percent solution with methanol, was reacted in a pressure-resistant reaction vessel with hydrogen at a pressure of 15,000 pounds per square inch for a period of two hours at a temperature of 270° C. using 2 percent by weight, based on contained copper, of the supported catalyst described above. A methyl acetate conversion of 89.5 percent was obtained with an efficiency to methanol and ethanol of 91.4 percent and 96.4 percent, respectively. The production ratio based on the methanol and ethanol recovered was equivalent to 175 pounds of product per cubic foot of catalyst volume per hour.

Example II

Methyl acetate, as an 82 percent solution with methanol, was reacted in a pressure-resistant reaction vessel with hydrogen at a pressure of 10,000 pounds per square inch for a period of two hours and at a temperature of 270° C. using 3 percent by weight, based on contained copper, of the supported catalyst described above. A methyl acetate conversion of 81.8 percent was obtained with an efficiency to methanol and ethanol of 82.6 percent and 83.5 percent, respectively. The production ratio based on the combined weight of methanol and ethanol produced was 90 pounds per cubic foot of supported catalyst per hour.

Example III

Approximately 350 grams of ethyl propionate were heated to 290° C. in a pressure-resistant vessel in the presence of 125 grams of the supported copper-chrome catalyst described above and under an initial hydrogen pressure of 5300 pounds per square inch. A temperature of 290° C. and a pressure of 15,000 pounds per square inch were maintained for a period of one hour. After the vessel and its contents had been cooled, the crude reaction product was discharged. Distillation and analysis of the fractions showed an ethyl propionate conversion of 80.4 percent and an efficiency to ethanol and n-propanol of 82.5 percent and 90.4 percent, respectively, based on the ethyl propionate charged. The production ratio based on the combined weight of ethanol and propanol produced was 125 pounds per cubic foot of supported catalyst per hour.

What is claimed is:

1. A process for the production of alcohols from esters which comprises reacting a lower aliphatic ester with hydrogen under hydrogenating conditions in the presence of a catalyst consisting of copper oxide promoted with chromium oxide and containing from 1 to 5 parts of chromium per 100 parts of copper.

2. A process for the production of methanol and ethanol which comprises reacting methyl acetate with hydrogen under hydrogenating conditions in the presence of a catalyst consisting of copper oxide promoted with chromium oxide and containing from 1 to 5 parts of chromium per 100 parts of copper.

3. A process for the production of ethanol and propanol which comprises reacting ethyl propionate with hydrogen under hydrogenating conditions in the presence of a catalyst consisting of copper oxide promoted with chromium oxide and containing from 1 to 5 parts of chromium per 100 parts of copper.

4. A process of the production of alcohols from esters which comprises reacting a lower aliphatic ester with hydrogen at a temperature in the range 250° C. to 400° C. and a pressure in the range 5,000 to 15,000 pounds per square inch in the presence of a catalyst consisting of copper oxide promoted with chromium oxide and containing from 1 to 5 parts of chromium per 100 parts of copper.

5. A process for the production of methanol and ethanol which comprises reacting methyl acetate with hydrogen at a temperature in the range 250° C. to 400° C. and a pressure in the range 5,000 to 15,000 pounds per square inch in the presence of a catalyst consisting of copper oxide promoted with chromium oxide and containing from 1 to 5 parts of chromium per 100 parts of copper.

6. A process for the production of ethanol and propanol which comprises reacting ethyl propionate with hydrogen at a temperature in the range 250° C. to 400° C. and a pressure in the range 5,000 to 15,000 pounds per square inch in the presence of a catalyst consisting of copper oxide promoted with chromium oxide and containing from 1 to 5 parts of chromium per 100 parts of copper.

7. In a process of hydrogenating a lower aliphatic ester to the corresponding alcohol, the improvement which comprises reacting the lower aliphatic ester with hydrogen at an elevated temperature and pressure in the presence of a catalyst consisting of copper oxide promoted with chromium oxide and containing from 1 to 5 parts of chromium per 100 parts of copper.

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