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RECOVERING METALS FROM HYDROFORMYLATION PRODUCTS

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This invention relates to a hydroformylation process, and more particularly to a hydroformylation process in which the valuable cobalt catalytic material is recovered.

Recently a wide interest has developed in the so-called "hydroformylation process" which is also known as the "carbonylation process" or the "oxonation of olefins." In this process a charge comprising carbon monoxide, hydrogen and an olefin is contacted with a cobalt hydroformylation catalyst, such as elemental cobalt or a cobalt salt, thereby yielding a liquid phase aldehydic product. Concomitantly, at least a portion of the cobalt hydroformylation catalyst is converted into cobalt carbonyl which remains dissolved in the liquid phase hydroformylation product. In addition to the cobalt carbonyl, the hydroformylation product may contain minor quantities of other cobalt substances such as colloidal cobalt metal, and cobalt hydrocarbonyl. In addition to the aldehydic constituents, and the dissolved cobalt carbonyl, the hydroformylation product also contains minor proportions of alcohols, acetals, and other organic compounds, plus unreacted charge.

In view of the high cost and short supply of cobalt it is very desirable to recover the cobalt contained as cobalt carbonyl in the hydroformylation product. Moreover, it is also advantageous to remove any additional metallic carbonyls such as iron carbonyl, and minor amounts of the carbonyls of nickel, chromium, and molybdenum, which may be present in the product stream as a result of processing equipment corrosion. In addition to the foregoing, it is desirable to ensure the removal of the cobalt carbonyl and metallic carbonyls from the hydroformylation product since these substances confer deleterious properties upon the hydroformylation product, such as rendering it very susceptible to condensation, polymerization and to oxidation. Furthermore, the aldehydic constituents of the hydroformylation product are frequently catalytically hydrogenated. The presence of dissolved cobalt carbonyl and other metallic carbonyls in the hydroformylation product adversely retards its catalytic hydrogenation inasmuch as the carbonyls decompose and give off carbon monoxide during the hydrogenation. This evolved carbon monoxide poisons most hydrogenation catalysts by greatly reducing their hydrogenating activity. In addition to the foregoing there is a concomitant deposition of elemental cobalt and other metals from the decomposed carbonyls which serves to plug the hydrogenator transfer lines, or more seriously, to plug and coat the hydrogenation catalyst bed.

The process of our invention deals with a hydroformylation process in which the cobalt is recovered. This is accomplished by hydroformylating an olefin with carbon monoxide and hydrogen by contact with a cobalt hydroformylation catalyst, thereby forming a liquid phase hydroformylation reaction product containing dissolved cobalt carbonyl. This liquid product is contacted with a heated, combustible, porous, carbonaceous support such as charcoal, coke, activated carbon and the like and the cobalt carbonyl is thereby decomposed into elemental cobalt and deposited upon the support. The support containing deposited cobalt is then ignited and the cobalt recovered. The process of our invention also permits the removal of other dissolved metallic carbonyls such as iron carbonyl, which may be present in the hydroformylation product, since these substances will also deposit the metal upon the support, from which it can be recovered by ignition of the support. In this manner the deleterious consequences arising from the presence of cobalt carbonyl and metallic carbonyls in the hydroformylation product are eliminated.

As an example of the process of our invention, a hydroformylation charge material comprising carbon monoxide, hydrogen, and an olefin (olefins with from 4 to 16 carbon atoms are preferred although other olefins may be successfully employed) is hydroformylated through contact with a cobalt hydroformylation catalyst. A wide variety of cobalt hydroformylation catalysts can be used. Examples of useful cobalt hydroformylation catalysts include: the so-called "Fischer-Tropsch" catalyst comprising metallic cobalt plus minor amounts of metallic oxides such as magnesia and thoria on a kieselguhr or other type base; cobalt salts such as the cobalt salts of aliphatic carboxylic organic acids of less than about 13 carbon atoms like cobalt acetate, cobalt 2-ethylhexanoate and cobalt naphthenate.

A wide variety of hydroformylation reaction conditions and procedures are applicable. Thus successful results can be secured over the temperature range of between about 100° to 600° F. and the pressure range of between about 750 to 10,000 pounds per square inch. However, hydroformylation is preferably carried out at selected temperatures within the range of about 260° to about 440° F. Optimum results are obtained when the temperatures are selected from the range of about 340° to about 380° F. Likewise the best results are secured when the pressure is in the range of 1500 to 7500 pounds per square inch, and the synthesis gas contains hydrogen and carbon monoxide in a mol ratio from about 0.5:1 to 8:1, the total pressure and the composition of the gas being selected to obtain a carbon monoxide partial pressure from about 750 to about 4000 pounds per square inch. Especially preferred results are obtained with a total pressure from about 3000 to about 4500 pounds per square inch and a synthesis gas having a mol ratio of hydrogen to carbon monoxide of about 1:1, the partial pressure of carbon monoxide being about 1500 to about 2250 pounds per square inch. Moreover, any of the conventional hydroformylation reaction procedures can be employed. Thus the charge can be passed through a fixed bed of cobalt hydroformylation catalyst, or alternatively, a suspension of cobalt hydroformylation catalyst in the charge procedure can be employed. However, the preferred procedure comprises dissolving a soluble cobalt hydroformylation catalyst such as the cobalt salt of an aliphatic carboxylic organic acid in the olefin constituent of the charge, and then hydroformylating the catalyst-charge mixture. In this type of process, the cobalt salt is at least largely converted to cobalt carbonyl during the hydroformylation reaction.

The effluent from the hydroformylation reaction is cooled and depressurized so as to condense the product aldehydes and alcohols, and release any unreacted entrained carbon monoxide and hydrogen. The optimum temperature and pressure to which the product should be subjected are dependent upon the charge, process equipment, etc., and can readily be determined by the operator through a few trial runs. The released carbon monoxide and hydrogen may be recycled for further use as a hydroformylation charge material.

The cooled and depressured hydroformylation product containing cobalt carbonyl, and possibly some additional metallic carbonyl, such as iron carbonyl originating from

processing equipment corrosion, is then contacted with a heated, combustible, porous support such as a porous carbonaceous support like charcoal, coke, activated carbon, etc. This results in the decomposition of the cobalt carbonyl and the iron carbonyl into elemental cobalt and iron, and a simultaneous deposition of this elemental cobalt and iron upon the support. The temperature to which the combustible, porous, carbonaceous support must be heated in order to decompose the cobalt carbonyl and any dissolved metal carbonyls depends upon a number of factors such as the relative amount of cobalt carbonyl to metallic carbonyl, the partial pressure of carbon monoxide in the system, the absolute temperature and pressure upon the hydroformylation product, etc. The temperature required to decompose cobalt carbonyl is somewhat lower than that required for iron carbonyl. Thus, if the hydroformylation product has been depressurized to about one atmosphere and the sole contamination is due to the presence of cobalt carbonyl, the requisite temperature to which the porous carbonaceous support must be heated is of the order of 165° to 212° F. On the other hand, if appreciable amounts of iron carbonyl are present, it is necessary to heat the porous carbonaceous support somewhat higher, such as to a temperature of between about 340° to 420° F. so as to decompose the iron carbonyl at this pressure. At other pressures and conditions, the carbonyl decomposition temperatures will vary somewhat, but can be accurately ascertained by a few simple trial runs. For example, at higher pressures, it will generally be desirable to operate at somewhat higher temperatures than those mentioned above.

After the cobalt has been deposited upon the combustible, porous, carbonaceous support, the support is removed from the system and ignited. After the ignition, the cobalt is recovered as cobalt oxide and/or metallic cobalt and may be reprocessed for further use by conventional processing methods. Thus, if the formation of a cobalt salt is desired, the recovered cobalt may be treated with a salt-forming acid and the resultant cobalt salt purified by recrystallization.

As an example of the application of the process of our invention, mixed octenes and a synthesis gas comprising a 1:1 molar mixture of hydrogen and carbon monoxide, were contacted for 15.7 minutes in an elongated reaction zone with a cobalt 2-ethylhexanoate hydroformylation catalyst dissolved in the octenes at a rate of 85,580 standard cubic feet per hour of synthesis gas per thousand gallons per hour of mixed octenes. The hydroformylation reaction temperature was 350° F. and the reaction pressure 3500 pounds per square inch. This operation yielded a hydroformylation product containing a major amount of nonyl aldehyde, and a minor amount of aldols, alcohols, and other organic compounds; and also containing about 0.5 milligrams of cobalt per milliliter of product, largely in the form of cobalt carbonyl.

This hydroformylation product was cooled to a temperature of 75° F., and depressurized to atmospheric pressure, and the entrained unreacted carbon monoxide and hydrogen removed. The hydroformylation product was then passed downwardly through a tower containing granules of activated carbon ranging in size from about 4 to 14 mesh. Simultaneously, steam was passed upwardly through the tower to give a temperature of 375° F. at the bottom of the tower, and about 70° F. at the top. By this procedure, cobalt carbonyl from the hydroformylation product was simultaneously decomposed and deposited upon the activated carbon in the form of elemental cobalt metal. The cobalt was then recovered by ignition of the activated carbon. A quantitative chemical analysis of the decobalted hydroformylation product revealed that it contained but 0.0007 milligram of cobalt per milliliter.

While the foregoing constitutes the preferred operating procedure for the process of our invention, it is to be understood that any modifications readily apparent to one skilled in the art can be utilized and that these modifications are to be considered as included within the appended claims. By way of example, it may sometimes be advantageous to remove the cobalt carbonyl and any metallic carbonyls from the hydroformylation product before removing the entrained unreacted carbon monoxide and hydrogen.

The process of our invention accomplishes efficient recovery of the valuable cobalt catalytic material contained in the hydroformylation product with a resultant saving in catalyst inventory. Moreover, it also prevents the deleterious effects which are concomitant with the presence of this material in the product. Thus, a more oxidative-resistant and condensation-resistant hydroformylation product is thereby obtained. In addition, the hydroformylation product may be catalytically hydrogenated more advantageously, since the catalyst-poisoning effect due to the presence of carbonyl compounds in the product is eliminated. Concomitantly, plugging of the hydrogenator due to the deposition of elemental metal from dissolved cobalt carbonyl and metallic carbonyls in the hydroformylation product upon the hydrogenation catalyst and/or the hydrogenator transfer lines is likewise eliminated.

We claim:

1. A process which comprises hydroformylating a charge comprising carbon monoxide, hydrogen and an olefin with a cobalt hydroformylation catalyst at selected temperatures within the range of about 260° to about 440° F. and a selected pressure in the range of about 1500 to about 7500 pounds per square inch, thereby forming a liquid hydroformylation product containing cobalt carbonyl, reducing the temperature and pressure on said hydroformylation product, passing said latter hydroformylation product downwardly through a demetalling zone containing a combustible, porous, carbonaceous support, passing steam upwardly through said demetalling zone to obtain a temperature of about 375° F. adjacent the bottom of said demetalling zone and a temperature of about 70° F. adjacent the top of said demetalling zone so as to decompose the cobalt carbonyl into elemental cobalt and deposit the same upon said support, and thereafter recovering the cobalt from said support.

2. A process which comprises hydroformylating a charge comprising carbon monoxide, hydrogen, an olefin having from 4 to 16 carbon atoms and iron carbonyl with a cobalt hydroformylation catalyst at a temperature of between about 340° to 380° F. and a pressure of between about 3000 to 4500 pounds per square inch, thereby forming a liquid phase hydroformylation product containing cobalt carbonyl and some iron carbonyl dissolved therein, reducing the temperature and pressure on the hydroformylation product, separating unreacted carbon monoxide and hydrogen from the hydroformylation product, passing said latter hydroformylation product downwardly through a demetalling zone containing a combustible, porous, carbonaceous support, passing steam upwardly through said demetalling zone to obtain a temperature of about 375° F. adjacent the bottom of said demetalling zone and a temperature of about 70° F. adjacent the top of said demetalling zone so as to decompose the cobalt carbonyl into elemental cobalt and the iron carbonyl into elemental iron and to deposit the cobalt and iron upon said support, igniting the support, and recovering the cobalt.

3. A process which comprises hydroformylating a charge comprising carbon monoxide, hydrogen, and an olefin with a cobalt hydroformylation catalyst in the presence of iron carbonyl at selected temperatures within the range of about 260° to about 440° F. and a selected pressure in the range of about 1500 to about 7500 pounds per square inch, thereby forming a liquid hydroformylation product containing cobalt carbonyl and iron carbonyl, reducing the temperature and pressure

on said hydroformylation product, passing said latter hydroformylation product downwardly through a demetalling zone containing a combustible, porous, carbonaceous support, passing steam upwardly through said demetalling zone to obtain a temperature high enough to decompose iron carbonyl adjacent the bottom of said demetalling zone and a temperature below the decomposition temperature of cobalt carbonyl adjacent the top of said demetalling zone so as to decompose cobalt carbonyl and iron carbonyl into elemental cobalt and elemental iron, respectively, and deposit the same upon said support, and thereafter recovering the cobalt from said support.

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