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(54) PRODUCTION OF SYNTHETIC PRODUCTS FROM CARBON MONOXIDE, HYDROGEN AND OLEFINS

(54) FABRICATION DE PRODUITS SYNTHETIQUES D'OXYDE DE CARBONE, D'HYDROGENE ET D'OLEFINES

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The invention relates to improvements in the production of aldehydes, alcohols and other synthetic products from reaction mixtures comprising carbon monoxide, hydrogen and olefins.

It is well known that by reacting olefins with water gas at temperatures of about 80°C. - 170°C. and at pressures of about 50-200 atmospheres, in the presence of a suitable catalyst, aldehydes are obtainable in good yields. Thus from mixtures of carbon monoxide, hydrogen and ethylene, it has been found possible to obtain propionaldehyde in yields of 65% based on the weight of ethylene employed. When using mixtures of carbon monoxide, hydrogen and cetene, a product has been obtained which, after hydrogenation to convert aldehydes to alcohols, gave C_{17} alcohols in 80% yield, based on the weight of cetene employed.

The catalysts usually employed, in the process have, hitherto, been solid cobalt-containing materials, a typical catalyst being one containing by weight 100 parts of cobalt, 5 parts of thoria, 9 parts of magnesia and 200 parts of Kieselguhr. Solid compounds of cobalt such as cobalt basic carbonates, cobalt naphthenate and cobalt salts of fatty acids have also been employed, generally in conjunction with a solid, porous reactor packing.

The use of a solid slurry catalyst gives a higher space-time yield than other prior OXO processes, but the use in general of solid catalysts is attended by a number of disadvantages. Thus the catalyst, usually in powder or granular form, must be mixed with the liquid feed and the slurry so formed pumped to high pressure. Furthermore, the method of the prior art necessitates a filtering stage for the recovery of the solid catalyst from the reaction product. The pumping and the filtering operations are both difficult and costly.

We have found that these disadvantages, which arise from the use of solid catalysts in the OXO reaction, are eliminated by the use of fluid catalysts as hereinafter described.

According to the invention, a catalyst for the OXO reaction is formed in a process which comprises contacting a cobalt-containing material with carbon monoxide at a pressure within a range of about 20-300 atmospheres and removing the fluid catalytic product obtained thereby. It is preferred that the fluid product be removed either as a solution in a suitable solvent or in admixture with a carrier gas. The temperature of the catalyst-generating reaction is generally maintained between 30°C. and 250°C.

If desired, instead of carbon monoxide alone, gaseous mixtures containing carbon monoxide may be employed. Where such mixtures are employed the partial pressure of carbon monoxide is maintained within a range of about 20 - 300 atmospheres.

Thus, instead of carbon monoxide alone, there may be used mixtures of hydrogen and carbon monoxide such as water gas, which are in general cheaper and more readily available. So called "blue water gas" is a particularly suitable gaseous mixture for use in the process of the invention. The preferred pressure range when using a carbon monoxide/hydrogen mixture is 50-250 atmospheres. Mixtures of carbon monoxide and hydrogen having a molar ratio in the range 1:3 to 1:0.5 are preferred, and particularly mixtures containing less hydrogen than corresponds to a

$CO:H_2$ ratio of 1:2.

The solution or gaseous mixture obtained according to the invention is suitable for direct use as a catalyst in the OXO reaction. By operating according to the process of the invention, the OXO reaction is carried out without dependence upon special solid cobalt catalysts of the type hereinbefore referred to.

The fluid catalyst according to the invention may be generated from any convenient source of cobalt, including cobalt metal, and readily-obtainable cobalt compounds such as cobalt oxide, cobalt carbonate or basic carbonate or cobalt sulphide. When metallic cobalt is used it is advantageous that the metal be either finely divided or dispersed over a suitable supporting material such as pumice or Kieselguhr. Cobalt oxide, and other solid compounds may, however be used in suitably-sized lumps, in pellet form, or in any other form convenient for charging to the vessel. Cobalt halides may be employed in the presence of a halogen acceptor, for example, metallic copper.

Cobalt recovered from products of the OXO reaction may be converted to a fluid catalytic material according to the process of the invention. It has also been found that cobalt which has been deposited in an OXO reactor is a suitable cobalt material for use in the present process.

The cobalt compound employed in the production of the fluid catalyst is usually subjected before use to reduction in the presence of hydrogen.

However, it is an important feature of the invention that in the use of cobalt oxide and carbon monoxide/hydrogen mixtures as the reactants for the process of the invention, a catalytic material is obtained without prior reduction of the cobalt oxide to metal. According to this feature of the invention catalytic materials for the OXO reaction are obtained from cheaper reactants and under milder and more economical conditions than have hitherto been considered feasible.

The fluid catalyst may be prepared in the form of a solution by the use of any solvent which is inert to the said catalyst and which will not prevent the subsequent use of the catalyst in the OXO reaction.

According to one method, the solvent and carbon monoxide-containing gas may be pumped concurrently or countercurrently, over a fixed bed of the cobalt-containing material.

Suitable solvents have been found to be hydrocarbons such as xylene, paraffins or cycloparaffins, ethers, esters, alkanols, such as octyl alcohol, and high-boiling products obtained in the OXO reaction. If desired the high-boiling products may be hydrogenated before being used as solvents for the purpose described.

According to one method of operation, for the production of a gaseous catalyst a vessel is packed with a cobalt compound and maintained at a temperature of between 30°C. and 250°C. A carbon monoxide-containing gas (advantageously water gas) is passed through the vessel to maintain the partial pressure of carbon monoxide within a range of about 20 - 300 atmospheres.

To produce a liquid catalyst, the above procedure is modified by simultaneously pumping a solvent through the vessel, when the catalyst is obtained as a solution in the solvent.

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When the fluid cobalt compound is to be employed as catalyst in the OXO reaction in the gaseous state, the carbon monoxide-containing gas is preferably a mixture of carbon monoxide and hydrogen having a molar ratio at least 1:2. Under these conditions these materials are present in the effluent gas from the catalyst-generating zone in suitable proportions for direct use in the subsequent synthesis.

This is not, however, essential since the proportions of $CO:H_2$ may be adjusted after catalyst generation by blending-in further carbon monoxide/hydrogen mixtures. Thus, if the catalyst-forming stage is operated to give a very high cobalt content in the effluent gas (for example, greater than 10mg./litre), the small amount of gas passed through the generation stage will have little effect upon the composition of the total gas feed to the OXO reactor.

When operating the catalyst regeneration zone, for the production of a gaseous phase product, in the temperature range of about 90-130°C., it has been found difficult to keep the cobalt content of the gaseous effluent constant, probably on account of the rapidity with which the cobalt content of the gas varies with temperature. Marked variations in the cobalt content of the gas are obviously inconvenient when the product is required for continuous use in the OXO reaction, since the OXO reaction rate is roughly proportional to cobalt concentration, which in turn has an effect on the reaction selectivity. When feeding gas direct from a catalyst producing zone to an OXO reaction zone it is therefore preferred to operate the catalyst-producing zone at temperatures below 80°C. or above about 130°C., since constancy of cobalt injection rate is more readily obtained in these ranges.

If desired however, a gaseous product obtained in the catalyst-forming reaction may subsequently be dissolved in a solvent and the solution employed as catalyst in the OXO reaction. Furthermore, solvents may be employed which would be unstable under the conditions of the catalyst-forming reaction. By this method the advantages attending the use of a solvent are retained while obtaining the advantages of the vapour phase generation of the catalyst.

By operating in this manner it is not necessary to pass the effluent gas from the catalyst regeneration zone to the OXO reaction zone, and carbon monoxide gaseous mixtures/which are not particularly suitable for use in the OXO reaction may be employed. Thus fluid cobalt catalysts have been successfully produced from gases having a hydrogen content of 2 - 66%. However it appears that the partial pressure of the cobalt compounds in the effluent gas is very roughly proportional at constant temperature to the carbon monoxide partial pressure, so that production ratio would be small with gases of very high hydrogen contents (for example, over about 70%), or alternatively very high total pressures would be needed to effect the reaction.

A suitable carbon monoxide/hydrogen mixture is obtained from effluent from the OXO reaction zone in which the hydrogen content is higher than in the feed thereto. The effluent from the catalyst-generation zone is preferably scrubbed for the removal of solid cobalt compounds and this stage can be combined with the scrubbing of the effluent gas from the OXO reaction stage with economy of equipment.

Furthermore fluctuations in the cobalt content of the catalyst passed to the OXO reactor may be avoided since the solutions so prepared can be bulked and a catalyst of constant cobalt content thus obtained.

The invention includes within its scope the application of the new and improved catalyst to the OXO reaction. Thus according to this aspect of the invention, synthetic products are produced from carbon monoxide, hydrogen and olefins by a process which comprises contacting carbon monoxide or a suitable gaseous mixture containing carbon monoxide with a solid cobalt compound or cobalt metal in a catalyst-generating zone at a temperature within the range 30 - 250°C. and at a partial pressure of carbon monoxide of 20 - 300 atmospheres, in the presence of absence of a solvent, and passing the product of this zone to an OXO reaction zone operated without the introduction of solid cobalt compounds in which an olefin is contacted with carbon monoxide and hydrogen at an elevated temperature, such as 100°C. - 180°C., and at a pressure of at least 50 atmospheres for the production of synthetic products. The preferred pressure range in the OXO reaction zone is 50 - 250 atmospheres and more particularly 100 - 200 atmospheres.

\ Either the catalyst-generating zone or the OXO reaction zone may be operated continuously or batchwise.

Preferably the catalyst and olefin feed rates are adjusted to maintain the weight of cobalt (estimated as metal) between 0.01% and 5%, preferably between 0.05% and 2%, of the weight of the olefin feed to the OXO reaction zone.

Cobalt contained in the effluent from the OXO reaction zone may be recovered according to conventional practice in operating the OXO reaction and if desired, recycled to the catalyst-generating zone. Thus the liquid product from the OXO reaction may be passed over a porous material (suitably pumice, Kieselguhr, silica-gel or active charcoal) at elevated temperatures in the presence of hydrogen whereby the cobalt is retained upon the porous material. The cobalt-containing porous material may then be treated in the catalyst-generating zone.

It has been found that the cobalt in the effluent from the OXO reaction zone may be recovered without hydrogen treatment if the product is subjected to a temperature in the range 120°C. - 250°C. and a pressure of 50 - 500 lbs./sq.in. for a period of time of at least 10 minutes.

For butyraldehyde production, operation of this stage at a temperature in the range 150°C.-200°C. and at a pressure of about 200 - 300 lb./sq.in. is preferred.

If it is desired that the aldehyde contained in the OXO reaction product should remain substantially unchanged during the recovery of the cobalt, the temperature of this treatment should be in the range 80°C.-120°C. and the pressure of hydrogen should not exceed 100 atmospheres.

If, however, it is intended to convert the aldehydes to alcohols, more drastic conditions may be employed, such as temperatures up to 200°C. and hydrogen pressures up to 200 atmospheres or more.

In general, it is preferred that contact time in the cobalt-recovery stage should not exceed 10 minutes and preferably 5 minutes, as in this way loss of aldehydes by condensation reactions is reduced.

With feedstocks yielding relatively low

boiling products, for example feestocks consisting of ethylene, propylene, and/or butenes, a modification of the above procedure is practicable. In this case the liquid reaction product is passed to a flash distillation stage, in which the aldehyde products are flashed overhead. The stage is preferably operated at a still-temperature not exceeding 50°C., if necessary operating under reduced pressure. The operation is generally accompanied by at least partial decomposition of the fluid cobalt compounds present although propionaldehyde may be removed without decomposing the catalyst. The residue from this flash distillation is then passed to the cobalt-recovery stage. Since the aldehyde product has already been recovered, the cobalt-recovery stage can then be operated under the more drastic conditions indicated above. The cobalt-free liquid effluent from this stage may then be used as reaction medium or solvent, either with or without further hydrogenation. Alternatively the residue from the flash distillation stage, containing suspended cobalt, can be treated with carbon monoxide under the conditions indicated, regenerating the catalyst in solution.

As the exit gas from the OXO reactor may contain significant amounts of fluid cobalt compounds, it is economical to scrub this exit gas in conventional manner with either fresh olefin feed or reaction medium in order to recover this cobalt in solution for re-use.

In the case where the feedstock is a lower olefin such as ethylene, propylene or butenes, the exit gas may also contain significant amounts of unreacted olefin. By operating this scrubbing stage with the reaction medium under pressure, this olefin may be recovered with the cobalt, and returned in solution to the reaction with fresh feed.

As in practice the generation of catalyst from recovered cobalt and from fresh cobalt is conveniently carried out in the same vessel or stage, it has been found advantageous that a cobalt-containing compound be used as the material on which the cobalt is deposited. Cobalt oxide can suitably be used for this purpose. Reduction of the oxide and hydrogen treatment of the recovered cobalt can thus be effected in one operation. In this case it is advantageous to pack the effluent end of the recovery vessel with absorbent or filtering material, in order to avoid carry-over of solid particles from the oxide or other cobalt compounds with the effluent.

An additional advantage of this method of operation is as follows: When cobalt is recovered on a porous support such as pumice, bauxite, or activated alumina, the cobalt can be re-converted to fluid catalyst by the methods outlined. Whilst the rate of catalyst production from such materials is reasonably constant over a substantial part of the operation, a significant fall in the rate of catalyst formation occurs during the re-conversion of the last portions of the recovered cobalt (about the last 30%, but varying somewhat with the conditions). This fall in the rate of catalyst formation can, however, be avoided by depositing the cobalt on a cobalt compound, or alternatively on a mixture of cobalt compound and porous support. The method thus provides yet another means of maintaining the cobalt-input rate substantially constant, whilst in this case obtaining the maximum possible reconversion of recovered cobalt to fluid catalyst.

As stated above it has been found that the cobalt recovered in the cobalt-recovery zone is often in a form which is only slowly converted to fluid catalyst. It has been found, however, that the rate of catalyst formation is greatly increased by treating such recovered cobalt with hydrogen at 150°C.-400°C. and at low pressures (suitably around 1 atmosphere) prior to conversion to catalyst.

According to one method of operation two reactors, packed with a porous material, are employed alternately for cobalt recovery and catalyst regeneration. Preferably both stages are operated at substantially the same temperature and preferably within the range 130°C.-250°C.

It will be understood that either the vapour phase method or the method using a solvent may be used in converting recovered cobalt back to catalyst.

The invention is illustrated but in no way limited by the following examples:-

Example 1.

This example illustrates the production of a liquid catalyst according to the invention.

Cobalt carbonate was precipitated from an aqueous solution of the nitrate in the presence of Kieselguhr, and the precipitate water-washed, dried at 110°C., granulated and packed into a steel reactor. The cobalt was reduced to metal in a hydrogen stream at 400°C. After cooling in hydrogen to 110°C., xylene was pumped over the mass at a rate of 1 volume per volume of cobalt-Kieselguhr preparation per hour, water gas being simultaneously passed through at a pressure of 100 atmospheres. A solution containing 2.12 g. of cobalt per litre was obtained as product.

The rate of production of catalyst fell during this period, and the cobalt-Kieselguhr mixture was again treated with hydrogen. After cooling, production was resumed but the water gas was replaced by carbon monoxide. The pressure was 100 atmospheres, xylene rate 2 volumes per volume of cobalt-Kieselguhr per hour, the temperature being 120°C. A solution was obtained containing 3.36 g. of cobalt per litre in nine hours operation.

Example 2.

This example illustrates the production of a gaseous catalyst according to the invention.

In this example the reduced cobalt-Kieselguhr composition described in Example 1 was used. The conditions and results obtained were as shown in the following Table:

Temperature °C.	Pressure lbs/sq.in. gauge.	Gas rate V/V/hour	Cobalt content of exit gas mg/ltr. (at 20°C. and 760 mms.)
85	1310	32 250	1.2 1.2
100	1495	104 24 180	4.0 4.0 4.6

Gas volumes are measured at 20°C. and 760 mms.

Similar results were obtained on replacing the cobalt-Kieselguhr composition by cobalt oxide, the oxide being reduced with hydrogen at 400°C. prior to use. The cobalt content of the gas stream with a water gas pressure of 1340 lbs./sq. in., a reactor temperature of 79°C. and a gas rate of 135 v./v./hour, was 4.7 mg./litre of gas.

Example 3.

This example illustrates the batchwise operation of the OXO reaction using the liquid catalyst according to the invention.

Octene-1 was charged to a stirred batch autoclave and liquid catalyst, prepared as described in Example 1, and containing 4.4 g. of cobalt per litre of solution, was added. The cobalt so charged (estimated as metallic cobalt) was 0.05 per cent. by weight of the octene-1 charged. Water gas was then added, and the reaction with the olefin occurred at 150°C. and at a water gas pressure of 110 atmospheres. The reaction was stopped after 100 minutes. Fluid cobalt compounds in the product were decomposed with hydrogen at 96°C.-114°C., the hydrogen pressure being 50-58 atmospheres. The filtered cobalt-free product was then hydrogenated on Raney nickel at 150°C. and 100 atmospheres of hydrogen. Analysis of the hydrogenated product showed that after allowing for the octyl alcohol added as catalyst solvent, 11 per cent. of the octene-1 had reacted to form aliphatic alcohols.

Example 4.

This example illustrates the operation of the OXO reaction in a continuous producer using a liquid catalyst, and an OXO reactor containing non-absorbent packing.

A steel tube was packed with steel rings. Through this tube propylene was fed concurrently downwards with water gas, and a solvent catalyst in xylene, prepared according to Example 1. In all of the tests the xylene and propylene feed rates were kept substantially constant, about 2 volumes of xylene per volume of liquid propylene being pumped through. The water-gas rate was such that about 1.6 mols. of carbon monoxide per mol. of propylene feed were passed through. The reaction temperature was 135°C. and the total pressure 100 atmospheres. The residence time of the liquid feed in the reactor was about 10 minutes. The results obtained for the variation of butyraldehyde production rate with amount of cobalt added were as follows:-

Cobalt added, wt. per cent. of propylene fed (estimated as metallic cobalt).	Butyraldehyde Production rate, g./hr.
0.13	2.0
0.2	2.1
0.4	7.2
0.47	9.0
0.53	8.8
1.06	10.7
1.8	14.8
2.2	15.8

A proportion of the cobalt separated in the reactor in insoluble form. This was recovered by treating the reactor with carbon monoxide at a temperature of 125°C.-135°C. and at a pressure of 50 atmospheres, pumping xylene through the reactor. The product was suitable for use as recycle catalyst and was used as a catalyst in the following example 5.

Example 5.

This example illustrates the use of a solid absorbent packing in the OXO reactor, with a liquid catalyst.

The steel ring packing used in Example 4 was replaced by dried, granulated Kieselguhr. Running under otherwise the same conditions as in Example 4, but with liquid catalyst addition at a rate of 0.7 per cent. by wt. of metallic cobalt on the olefin feed, a production rate of 11.5 g. of butyraldehyde per hour was obtained.

Example 6.

This example illustrates the operation of a cobalt-recovery zone.

The butyraldehyde products obtained in Examples 4 and 5 were treated. These products from the OXO reactor were let down to atmospheric pressure after cooling, the bulk of the dissolved carbon monoxide being released (this step is not regarded as essential). The liquid was then pumped through a tube packed with granulated pumice concurrently with a hydrogen stream, the liquid-residence time being about 10 minutes. The conditions and degree of cobalt removal obtained were as follows:-

Temperature °C.	Pressure of hydrogen lbs./sq. in. gauge.	Wt. per cent. of cobalt in product removed.
100	447	97
99	360	96
99	311	92

Example 7.

This example illustrates the operation of a catalyst-recovery zone.

The cobalt recovered on pumice as described in Example 6 was used. This was treated with carbon monoxide at a pressure of 400 lbs./sq. in. gauge, xylene being pumped through at a rate of 1 volume per volume of pumice per hour, the temperature being 100°C. A catalyst solution in xylene was obtained containing 1.12 g. of cobalt per litre of solution.

By operating the OXO process as hereinbefore described considerable improvement is to be found over the methods of the prior art. Thus regulation of the rate of catalyst input is greatly facilitated with much better control of the reaction in consequence. Side reactions notably with the formation of high-boiling products, are materially reduced.

Example 8.

This example illustrates the use of a reduced cobalt oxide for the production of a gaseous catalyst according to the invention.

90 g. of granular commercial black oxide of cobalt were charged to a high pressure reactor, and reduced with hydrogen at a temperature of 400°C. and at atmospheric pressure. Water gas containing 40 per cent. by volume of carbon monoxide was then passed through the high pressure reactor under various conditions of temperature and pressure. The cobalt content of the effluent gas was then determined, the results being shown in Table 4.

Table 4.

Temperature of Cobalt.	Gas Rate. Litres/Hour	Pressure pounds per square inch.	Cobalt Content of Exit Gas - mg. Cobalt per Litre of Gas.
82	8 17.3	1400	4.1
	16.2	1380	4.2
100	15.0	1500	10.9
	16.7	1414	10.2
	15.0	1365	9.1
	15.0	1300	8.9
125	14.4	1490	2.8
	17.1	1350	1.0
	14.7	1000	0.55
	16.2	500	0.06

Gas volumes given are those measured at 20°C. and 760 mm. of mercury. This example illustrates that the optimum production of cobalt derivatives volatilised in the gas stream is at temperatures in the region of 100°C. when operating with a total pressure of about 1500 pounds per sq. in., and also that pressures in the region of 500 pounds per sq. in. give very low production rates.

Example 9.

The materials and method used here were similar to those used in Example 8. The results illustrate the fact that at low temperatures the cobalt content of the gaseous effluent was very little affected by gas rate. The results are shown in Table 5.

Table 5.

Temperature °C.	Gas Rate Litres/ Hours.	Pressure lbs./sq. in.	Cobalt Content of Exit Gas -mg./ litre.
104 - 105	10.6	1450	10.6
	12.6		10.1
	17.5		10.3
	30.8		12.3
	48.0		10.9

During these tests about 60% of the cobalt charged to the reactor was volatilised in the gas stream, with a fall of only about 20% in the rate of production of volatile derivatives under the same conditions.

Example 10.

In this example, using the same method as in Examples 8 and 9, but employing the cobalt oxide without prior reduction, it was found that a satisfactory rate of production of volatile derivatives of cobalt was possible. The results are shown in Table 6.

Table 6.

Temperature °C.	Gas Rate Litres/ hour.	Pressure lbs./sq. in.	Cobalt Content of Exit gas - mg. per litre.
99	15.5	1530	5.2
99	15.3	1465	4.3

Operation for a few hours was required before the cobalt content of the exit gas rose to the values shown. Prior to this, nickel and iron (present as impurities in the cobalt oxide) were predominant in the volatile metallic compounds produced.

Example 11.

This example illustrates the production of a gaseous-phase cobalt catalyst in the temperature range 35°C.-80°C. and in the temperature range 130°C.-250°C.

Water gas containing 35% of carbon monoxide was passed over reduced cobalt oxide (1 volume) at a pressure of 3,000 lbs. per sq. in. gauge, the gas-feed rate being 1400 volumes/hour (measured at 20°C. and 760 mm.)

	Example 1.	Example 2.
Temperature, °C.	38	210
Cobalt content of gas, mg./litre	0.7	0.2

Example 12.

This example illustrates the production of gaseous-phase cobalt catalyst using a feed gas containing carbon monoxide and hydrogen in the molar ratio 1:3.

Charge: 200 g. of black cobalt oxide in $\frac{1}{8}$" pellets.
Feed Gas: Mols. % CO = 22.
Mols. % H_2 = 66.
Temperature: 126°C.
Pressure: 1335 pounds per sq. in. gauge.
Gas Rate: 39 litres/hour (measured at 20°C. and 760 mm.)

After passing the feed gas over the oxide for a few hours under these conditions, the effluent gas was found to have a cobalt content of 2.3 mg./litre.

Example 13.

This example illustrates the production of a liquid catalyst from reduced cobalt oxide.

The solvent used was xylene. 330 grams of black oxide of cobalt in the form of pellets was charged to the reactor and reduced with hydrogen at a temperature of 400°C. and at atmospheric pressure. Xylene was then pumped over the cobalt at 200 ccs./hour concurrently with water gas at a pressure of 1500 pounds per square inch. In this Example the temperature was 125°C., and 5 litres of solution, containing 1 g. of cobalt (estimated as metal) per litre were prepared. The concentration of cobalt in the solution produced fell continuously during the test. This fall was less rapid with a reaction temperature of 110°C.

Example 14.

The conditions employed were the same as for Example 13, except that 2-ethylhexanol was used as solvent, and the temperature was maintained at 115°C.-120°C. The solution obtained contained 4.4 g. of cobalt per litre.

Example 15.

Using the method of example 13, xylene (500 ccs./hr.) was pumped concurrently with water gas over 300 grams. of cobalt. With a pressure of 1500 pounds per sq. inch and a temperature of 115°C. 14 litres of solution containing 2.3 g. of cobalt per litre were obtained.

On raising the pressure to 3000 pounds per sq. inch with the same reaction temperature, 9 litres of solution containing 10.6 g. of cobalt per litre were obtained.

Example 16.

This example illustrates the conversion of gas-phase cobalt catalyst to solution, and the use of the solution in the OXO reaction.

Cobalt catalyst-containing gas was made by the method of Example 12. Cobalt was washed from the gas by a scrubbing operation of conventional type at room temperature with di-isobutylene. A solution of catalyst in di-isobutylene was thus obtained. The concentration was adjusted by dilution with fresh olefin, and tests carried out pumping the solutions so obtained through a coil reactor with water gas. The conditions used, and the C_9 aldehyde-production rates obtained, are shown in the following Table 7:-

Table 7

Temperature, $^{\circ}$C.	150	151	149	150
Pressure, lbs.per sq. in gauge.	1500	1500	1480	1500
Cobalt concentration, g./litre.	0.70	1.3	0.42	0.06
Aldehyde production rate, g./hour/litre reaction space.	42	82	46	26

It should be noted that with this method, organic peroxides are advantageously removed from the solvent for the catalyst, otherwise partial precipitation of cobalt may occur.

Example 17.

This example illustrates the use of a gaseous-phase catalyst for the OXO reaction on octene-1.

Volatile derivatives of cobalt were produced by the vapour-phase method, reacting water gas (containing 35% of carbon monoxide) at a temperature of 75°C. and under a pressure of 1500 pounds per square inch with cobalt oxide. These derivatives sublimed in the water gas stream directly into a reaction zone into which octene-1 was pumped at a rate of 0.9 volumes per volume of reaction space per hour. The water gas was added in about 50 per cent. by weight excess of that required for reaction of all the olefins. The reaction of the olefin in this stage is carried out at a temperature of 135°C.-138°C. and at a pressure of 1400 pounds per square inch. 70% of the olefin feed reacted, giving a product, which on hydrogenation furnished a yield of nonyl alcohols, equal to 60-70% by weight on the total olefin feed. The cobalt added in the water gas stream was equivalent to 0.2% by weight of the total olefin feed.

Example 18.

This illustrates the production of a catalytic solution from solid cobalt compounds deposited in a reactor during a continuous process in which olefin and water gas were reacted to produce aldehydes. The reaction for the preparation of a catalyst according to the invention was carried out with water gas in the presence of xylene as solvent. The amount of cobalt present in the reactor is about 5 grams dispersed on a Lessing Ring packing, 300 ccs. in volume. Xylene (100 ccs. per hour) and water gas were pumped through this reactor the temperature being 120°C. A decline in catalyst-formation rate occurred in over 4 hours, as shown in the following figures.

Hours on stream	1	2	3	4
Cobalt in solution g./litre.	0.53	0.52	0.35	0.28

Reaction at 130°C. under otherwise similar conditions, after treating the deposited cobalt with hydrogen at 200°C. gave the following results.

Hours on stream	1	4
Cobalt in solution g./litre.	0.42	0.17

The greater rate of decline in catalyst-formation rate at 130°C. as compared with 120°C., is apparent.

By operating the OXO process as hereinbefore described considerable improvement is to be found over the methods of the prior art. Thus regulation of the rate of catalyst-input is greatly facilitated with much better control of the reaction in consequence. Side reactions, particularly the formation of high boiling products are materially reduced.

Example 19.

Using the same conditions as for Example 13, but replacing the xylene by desulphurised White Spirit fraction from petroleum consisting mainly of paraffin and naphthene hydrocarbons, a solution of cobalt catalyst was obtained containing 2.34 gs. cobalt per litre.

Example 20.

This example illustrates the deposition of cobalt from the OXO reactor on to cobalt oxide.

Charge to Reactor

Cobalt oxide (⅛" pellets)	50 ml.
Pumice	50 ml.

Feedstock

Crude butyraldehyde xylene mixture, products from the OXO reaction on propylene in xylene as solvent.

This was pumped downwards over the cobalt oxide-pumice mixture under conditions and with the results shown in the following Table 8:-

Table 8.

Period	1	2	4
Liquid feed ml./hour	950	1400	1475
Temperature, °C.	200	200	200
Pressure, pounds per square inch gauge.	260	200	260
Aldehyde in feed, wt. per cent.	46.6	18.6	18.6
Aldehyde in product, wt. per cent.	45.5	18.4	18.2
Cobalt in feed, g./litre.	0.88	0.46	2.76
Wt. per cent. cobalt removed.	97	93	98.5

15 g. of cobalt were recovered from the liquid product during these series of tests.

Example 21.

This example illustrates the recovery of cobalt from the OXO reaction product in the absence of a solid support and without hydrogen treatment.

Crude butyraldehyde products from the OXO reaction on propene, containing 85% of butyraldehydes and 0.3 g. per litre of cobalt were pumped through a steel pipe at a temperature of 200°C. and at a pressure of 200 pounds per square inch gauge and at a rate of 1 litre per hour, the pipe volume being 150 ml. The products were passed to a settling vessel, and cobalt-free liquid product, still containing 85% of butyraldehyde, drawn from the upper portion of this vessel through a lime filter, and passed to a free fractionator. A sediment of precipitated cobalt settled to the bottom of the vessel, and was periodically drained-off as a slurry from the base.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A continuous process for the production of synthetic oxygen-containing compounds in which aldehydes are produced in improved yields, which comprises contacting a solid cobalt compound with carbon monoxide and hydrogen in a catalyst-generating zone at a temperature within the range 30° - 250°C. and at a partial pressure of carbon monoxide of 20-300 atmospheres and continuously passing as fluid catalyst at least part of the product of this zone to an OXO reaction zone, together with a continuous feed comprising an olefin, carbon monoxide and hydrogen, said OXO reaction zone being operated at elevated temperatures and at a pressure in the range 50-250 atmospheres without the introduction of solid cobalt compounds, the feed rates of the fluid catalyst and olefin being adjusted to maintain the weight of cobalt, determined as the metal, in the feed between 0.01% and 2% based on the weight of the olefin in the feed.

2. A process according to claim 1, in which the solid cobalt compound is contacted with a mixture of carbon monoxide and hydrogen wherein the mol ratio is greater than 1:2

3. A process according to claim 1, in which the solid cobalt compound is selected from the group consisting of cobalt metal, cobalt oxide and cobalt carbonates.

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4. A process according to any one of claims 1 to 3, in which the olefin is propylene.

5. A process according to any one of claims 1 to 3, in which the cobalt is removed from the OXO reaction product by passage over aporous support in the presence of hydrogen.

6. A process according to any one of claims 1 to 3, in which the cobalt is removed from the OXO reaction product by subjecting the product to a temperature of 120° - 250°C. at a pressure of 50-500 lbs/sq.in. for at least 10 minutes.

7. A process according to anyone of claims 1 to 3, in which the cobalt is removed from the OXO reaction product by deposition on a cobalt-containing compound and wherein the recovered cobalt so obtained is employed together with the said cobalt-containing material for the generation of fluid cobalt catalyst by reaction with carbon monoxide and hydrogen.

8. A process according to any one of claims 1 to 3, in which effluent gas from the OXO reactor containing carbon monoxide and hydrogen is recycled to the catalyst generating zone.

9. A process according to any one of claims 1 to 3, in which the olefin contains 2-4 carbon atoms per molecule wherein the liquid product from the OXO reaction is passed to a flash distillation stage operated at a still temperature not exceeding 50°C. in which aldehydes are removed overhead and a cobalt-containing material recovered as residue.

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10. A process as specified in any one of claims 1 to 3, in which the olefin is a mono-olefin.

11. A process as specified in any one of claims 1 to 3, in which the olefin is an aliphatic olefin.

12. A process as specified in any one of claims 1 to 3, in which the olefin is a cyclic olefin.

13. A process as specified in claim 1, in which the catalyst generating zone is operated in the presence of a solvent which is inert to the catalyst and a liquid product is removed from the catalyst generating zone and fed to the OXO reaction zone.

14. A process according to claim 13, in which the solvent is selected from the group consisting of aromatic hydrocarbons, liquid olefins and high boiling products of the OXO reaction.

15. A process as specified in any one of claims 1 to 3, in which the temperature of the OXO reaction zone lies within the range 100°-180°C.

16. A process according to any one of claims 1 to 3, in which the cobalt is removed from the OXO reaction product by deposition on cobalt metal and wherein the recovered cobalt so obtained is employed together with the said cobalt metal for the generation of fluid cobalt catalyst by reaction with carbon monoxide and hydrogen.

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17. A continuous process for the production of synthetic oxygen containing compounds in which aldehydes are produced in improved yields, which comprises contacting cobalt metal with carbon monoxide and hydrogen in a molar ratio less than 1:0.5 and greater than 1:2 in a catalyst generating zone at a temperature within the range 30° - 250°C. and at a partial pressure of carbon monoxide of 20-300 atmospheres and passing as fluid catalyst at least part of the gaseous product, comprising volatile compounds of cobalt, to an OXO reaction zone operated in continuous manner and without the introduction of solid cobalt compounds and wherein an aliphatic mono-olefin is contacted with carbon monoxide and hydrogen at a pressure within the range 50-250 atmospheres and a temperature within the range 100° -180°C., the feed rates of the fluid catalyst and olefin being adjusted to maintain the weight of cobalt, determined as the metal, in the feed between 0.01% and 2% based on the weight of the olefin in the feed.

18. A continuous process for the production of synthetic oxygen-containing compounds in which aldehydes are produced in improved yields, which comprises contacting carbon monoxide and hydrogen with a solid cobalt compound in a catalyst-generating zone at a temperature within the range 30°-250°C. and at a partial pressure of carbon monoxide of 20-300 atmospheres, continuously passing, as fluid catalyst at least part of the product of this zone, in the gaseous phase, to an OXO reaction zone, together with

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a continuous feed comprising an olefin, carbon monoxide and hydrogen, said OXO reaction zone being operated without the intoduction of solid cobalt compounds and at elevated temperature and a pressure in the range 50-250 atmospheres, and the feed rates of the fluid catalyst and olefin being adjusted to maintain the weight of cobalt, determined as the metal, in the feed between 0.01% and 2% based on the weight of the olefin in the feed, and separating at least one aldehyde from the OXO reaction product.

19. A continuous process for the production of synthetic oxygen-containing compounds in which aldehydes are produced in improved yields, which comprises continuously contacting carbon monoxide and hydrogen with a solid cobalt compound in a catalyst-generating zone at a temperature within the range 30°-250°C. and at a partial pressure of carbon monoxide of 20-300 atmospheres, and continuously passing, as fluid catalyst, at least part of the product of this zone to an OXO reaction zone, together with a continuous feed comprising an olefin, carbon monoxide and hydrogen, said OXO reaction zone being operated without the introduction of solid cobalt compounds and at elevated temperature and a pressure in the range 50-250 atmospheres, and the feed rates of the fluid catalyst and olefin being adjusted to maintain the weight of the cobalt, determined as the metal, in the feed between 0.01% and 5% based on the weight of the olefin in the feed, and separating at least one aldehyde from the OXO reaction product.

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20. A process for the production of synthetic oxygen-containing compounds in which aldehydes are produced in good yields, in which a fluid cobalt carbonyl is used as catalyst and in which the overall losses of cobalt are small, which comprises contacting solid cobalt metal with a gas consisting at least in part of carbon monoxide in the absence of olefin feed in a first zone whereby a fluid cobalt carbonyl is formed, passing at least part of the said fluid cobalt carbonyl as catalyst through a second zone together with an olefin, carbon monoxide and hydrogen, the second zone being operated in continuous manner under the conditions of the OXO reaction, said fluid cobalt carbonyl being the sole catalytic material introduced into the secondzone, withdrawing from the second zone a mixture comprising synthetic oxygen-containing compounds and fluid cobalt compounds, contacting at least part of said mixture in a third zone with a solid support material under conditions for the decomposition of the fluid cobalt compound with deposition of cobalt metal upon the support and withdrawing the synthetic oxygen-containing compound from the third zone, and wherein the flow through the system between the zones is periodically reversed when depletion of cobalt in the first zone reaches a predetermined amount and conditions in the system adjusted so that a fluid cobalt carbonyl is produced in the third zone and fluid cobalt compounds are decomposed in the first zone, the feed rates of fluid

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cobalt carbonyl and olefin to the synthesis reaction zone being adjusted to maintain the weight of cobalt, determined as the metal, in the feed between 0.01% and 2.0% based on the weight of the olefin in the feed.

21. A process for the production of synthetic oxygen-containing compounds in which aldehydes are produced in good yields, in which cobalt compounds are used as catalyst and in which the overall losses of cobalt are small, which comprises contacting solid cobalt metal with carbon monoxide and hydrogen in the absence of olefin feed in a first zone at a temperature within the range 30° - 250°C and at a partial pressure of carbon monoxide within the range 20-300 atmospheres for the production of a catalyst composed predominantly of cobalt hydrocarbonyl, passing at least part of the product of the first zone, comprising cobalt hydrocarbonyl, as catalyst, through a second zone together with an aliphatic mono-olefin, carbon monoxide and hydrogen, the second zone being operated in continuous manner at a pressure within the range 50-250 atmospheres and a temperature within the range 100°-180°C, said fluid catalyst composed predominantly of cobalt hydrocarbonyl being the sole catalytic material introduced in the second zone.

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22. A process for the production of synthetic oxygen-containing compounds in which aldehydes are produced in good yields by the reaction of olefinic compounds with carbon monoxide and hydrogen, in which a fluid cobalt carbonyl is used as catalyst, which comprises contacting solid cobalt metal with a gas comprising carbon monoxide, in the absence of olefin feed, in a first zone whereby a fluid cobalt carbonyl is formed, passing said fluid cobalt carbonyl as catalyst through a second zone together with an olefin, carbon monoxide and hydrogen, the second zone being operated in a continuous manner under the conditions of the OXO reaction, said fluid cobalt carbonyl being the sole catalytic material introduced into the second zone, withdrawing from the second zone a mixture comprising synthetic oxygen-containing compounds and fluid cobalt compounds, contacting said mixture in a third zone with a solid support material under conditions for the decomposition of the fluid cobalt compound with deposition of cobalt metal upon the support and withdrawing the synthetic oxygen-containing compound from the third zone, and wherein the flow through the system between the zones is periodically reversed when a predetermined amount of cobalt has been deposited in the third zone and conditions in the system adjusted so that a fluid cobalt carbonyl is produced in the third zone and fluid cobalt compounds are decomposed in the first zone, the concentration of cobalt in the second zone being maintained within 0.1% to 0.3%.