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SYNTHESIS OF METAL CARBONYLS

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This invention relates to improvements in the manufacture of nickel and/or cobalt carbonyls, and more particularly to an improved process whereby these carbonyls are obtained at high space-time yields from metal salts and carbon monoxide.

The standard method for preparing metal carbonyls in the past has been by direct reaction between the carbonyl-forming metal, e. g., nickel, and carbon monoxide. This method has numerous disadvantages from a practical standpoint. For example, to obtain sufficiently high rates of production it is essential to employ an "active form" of the metal in a sufficiently fine state of subdivision. Moreover, other well-known difficulties, common to virtually all processes involving a reaction between a gas and a solid, are also encountered. A high pressure method for converting metal chlorides, bromides or iodides to metal carbonyls in solution has recently been proposed (Hieber, *Die Chemie*, vol. 55, pages 7-11 and 24-28, Jan. 3 and 17, 1942). In the latter process a free metal, which may constitute the autoclave wall or which may be introduced in the form of powder, reacts with a metal halide and with carbon monoxide to give a metal carbonyl. One disadvantage of this process is that it also requires an unduly long reaction time for the formation of appreciable quantities of the carbonyl, especially when the halide used is either the chloride or the bromide. Other processes for making nickel carbonyl and other metal carbonyls have been proposed from time to time, such as the direct treatment of nickel sulfide-containing mixtures with a carbonaceous material and carbon monoxide, preferably at high pressures. The latter processes, in general, are not well adapted to the synthesis of high quality nickel or cobalt carbonyl, such as is required, for example, in carrying out certain recently discovered catalytic reactions in the field of organic chemistry.

The need for improved methods for preparing and recovering nickel and cobalt carbonyls has become more important in recent years due to the discovery of these new uses for nickel and cobalt compounds in organic synthesis. The compounds which are of greatest value in this respect are nickel and cobalt compounds which are soluble in organic media, such as nickel and cobalt carbonyl, and various complexes thereof. Organic salts of nickel and cobalt are, of course, more readily and more safely transported than nickel and cobalt carbonyls, yet these metal carbonyls are frequently preferred over these salts because

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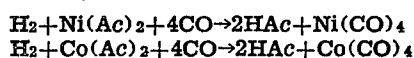
the carbonyls have physical properties (volatility, etc.) which make them extremely well adapted for use in reaction systems involving recovery and recycling of the catalyst. For example, it is disclosed in copending application S. N. 731,706 that nickel carbonyl can be removed from a crude reaction product (obtained by reacting a carboxylic acid with an olefin and CO) by vaporization in a stream of carbon monoxide, followed by scrubbing the effluent gas with an organic solvent such as propionic acid. In many instances this is a less costly operation than recovering a non-volatile nickel or cobalt salt from a reaction mixture or portion thereof (e. g. a tarry distillation residue).

An object of this invention is to overcome the disadvantages of the previously known processes for manufacturing nickel and cobalt carbonyls. Another object is to provide a novel method for making these carbonyls from readily available starting materials. Still another object is to obtain nickel or cobalt carbonyl at high space-time yields from nickel or cobalt salts and carbon monoxide. A further object is to obtain nickel or cobalt carbonyls from reaction mixtures initially containing dissolved, catalytically active nickel or cobalt organic salts in such form that the said nickel or cobalt carbonyl can be readily used as a recovered catalyst in the same or similar reaction mixtures. Thus, one of the objects is to provide a method for converting organic salts of nickel or cobalt to metal carbonyls, thereby taking advantage of the favorable characteristics of nickel and cobalt carbonyl catalysts (recoverability, ease of recycling, etc.), while at the same time avoiding the difficulties and dangers attending the manufacture and transportation of these carbonyls by previously known methods. Other objects of the invention appear hereinafter.

These objects are accomplished in accordance with this invention by reacting a nickel or cobalt salt of an organic carboxylic acid with carbon monoxide and hydrogen, whereby a mixture from which the desired metal carbonyl can be separated readily is produced. Best results are obtained by carrying out the said reaction at a pressure of 50 to 1200 atmospheres and a temperature of 100° to 375° C. in the presence of a liquid organic solvent for the metal carbonyl (e. g. an organic reaction mixture, in which both the said salt, and the said metal carbonyl, are effective as catalysts), thereafter cooling the resulting mixture to a temperature in the range of 50° to 100° C., passing carbon monoxide gas through the resulting liquid mixture at 50° to 100° C., and recovering the metal carbonyl from

the effluent carbon monoxide by absorption in a liquid organic solvent. The separation of the metal carbonyl from the solution in which it is formed is best accomplished by means of counter-current stripping with carbon monoxide under atmospheric pressure. The subsequent absorption of the metal carbonyl in the organic liquid solvent is preferably carried out at a temperature of -80° to $+10^{\circ}$ C., under about atmospheric pressure. Preferably the mol ratio of $H_2:Ni$ in the reaction mixture should be from 0.1 to 2.0 and the partial pressure of CO should be at least several atmospheres during the synthesis of the metal carbonyl. The mol ratio of $CO:H_2$ preferably should not be less than about 1:1, especially if the total pressure is below about 50 atmospheres. Outstanding results from a practical standpoint, are obtained at 175° to 320° C. under a carbon monoxide partial pressure of 100 to 1000 atmospheres, the initial mol ratio of $H_2:Ni$ being from 1:1 to 3:1, and the initial mol ratio of $CO:H_2$ being from 25:1 to 500:1. Best results are obtained when an organic liquid which is a solvent for both the metal salt and the metal carbonyl is employed, as a diluent. Suitable solvents include the liquid aliphatic carboxylic acids, as well as other common organic liquids such as esters, dioxanes, ketones, hydrocarbons, anhydrides and the like. It is, in certain instances, desirable that the solvent be inert towards carbon monoxide under the nickel carbonyl-forming conditions, but this, of course, does not preclude subsequent introduction of one or more substances which can undergo reaction in the presence of the metal carbonyl. For example, the lower aliphatic carboxylic acids, which are the preferred solvents employed in the practice of the invention, undergo reaction when heated under pressure with carbon monoxide and an olefin in the presence of soluble nickel compounds to form anhydrides of carboxylic acids, as disclosed in copending application S. N. 630,540; if, for example, nickel propionate is employed as a catalyst for the synthesis of propionic anhydride from propionic acid, CO and ethylene, the nickel can be recovered and recycled as nickel carbonyl, as disclosed herein. After the nickel carbonyl is returned to the reaction mixture, it may be in whole or in part, converted to nickel propionate by reaction with propionic acid, the extent of the conversion to nickel propionate being determined by the temperature and the carbon monoxide pressure. Thus, the present invention is particularly directed to the Ni or Co carbonyl-forming and recovery steps, in processes in which an organic reaction, catalyzed by the Ni or Co compounds, takes place subsequent to or simultaneously with the formation of the Ni or Co carbonyl.

The invention is based in part upon the discovery that nickel carbonyl and cobalt carbonyl can be produced in accordance with the following reactions,



wherein Ac represents the acid radical of an organic carboxylic acid. This is believed to be a novel reaction. Thus, it was indeed surprising to discover that hydrogen, in suitable quantities, is critically essential in the formation of nickel carbonyl or cobalt carbonyl from the organic salts and carbon monoxide. If, in the practice of the invention, less than one mol of hydrogen

is present per atom of Ni or Co the conversion of nickel or cobalt salt to nickel or cobalt carbonyl is limited because the quantity of hydrogen is stoichiometrically insufficient. A large excess is to be avoided, since this results in undesirable hydrogenation reactions taking place, and necessitates use of a relatively high pressure of carbon monoxide for complete conversion of Ni or Co to carbonyl. For these reasons the quantity of hydrogen present initially should be carefully controlled. Furthermore, in processes in which the nickel carbonyl or cobalt carbonyl is to be employed as a catalyst for a subsequent reaction involving the use of carbon monoxide, but not hydrogen, as a reactant, it is of course desirable to obtain the nickel or cobalt carbonyl in solution under a blanket of substantially hydrogen-free carbon monoxide, and for this additional reason it is ordinarily desirable to avoid too large an excess of hydrogen in the metal carbonyl-forming mixture, beyond the quantity stoichiometrically required for reaction with the Ni or Co in the nickel salt.

While any temperature within the range of 100° to 375° C. may be employed for the synthesis of the metal carbonyls in the practice of the invention, there is an advantage in employing temperatures which are sufficiently high to insure a rapid reaction rate, but not so high as to limit seriously the equilibrium concentration of nickel carbonyl or cobalt carbonyl which can be built up. Thus, the preferred temperatures are in the range of 250° to 320° , but somewhat higher temperatures may be employed if the partial pressure of carbon monoxide exceeds a few hundred atmospheres. At temperatures not exceeding about 300° to 330° C., good conversions to nickel or cobalt carbonyl can be obtained at partial pressure of carbon monoxide in the range of 100 to 1000 atmospheres. The variation of conversion with temperature and pressure is shown in the following table. To obtain the most satisfactory results from the standpoint of reaction rates, it is preferred to operate at the maximum temperatures at which the reaction equilibrium is favorable to high, or virtually complete, conversion to metal carbonyl, at the particular carbon monoxide pressure involved.

TABLE I

Conversion of nickel propionate to nickel carbonyl in propionic acid as solvent by reaction with CO in the presence of about two mols of H_2 per mol of nickel propionate

Conversion, Percent	Partial Pressure of CO (atm.)	Mol Ratio CO:Ni	Temperature, $^{\circ}$ C
92.1	100	1:0.0034	275
92.7	100	1:0.0034	290
65.5	100	1:0.0034	305
99.36	200	1:0.0024	330
99.5	300	1:0.03	268

The metal carbonyl can be separated from the mixture in which it is formed by contacting the said mixture with a stream of carbon monoxide-containing gas at a pressure of 1 to 5 atmospheres at a temperature high enough to render the metal carbonyl sufficiently volatile, yet not high enough to cause decomposition of the metal carbonyl. The temperature range within which this can be done is surprisingly narrow, e. g. about 50° to 100° C. Indeed, it is rather remarkable that these metal carbonyls can be removed from solution

without decomposition at any temperature under ordinary pressures, because distillation of these substances is generally attended by thermal decomposition to the free metal, unless a relatively low pressure is employed. Moreover, at low pressures, condensation of the distillate is difficult even at very low temperatures.

The minimum quantity of carbon monoxide which is required in stripping Ni or Co carbonyls from solutions thereof at about atmospheric pressure depends upon the temperature of the contents of the stripping column. This can be illustrated, in a specific embodiment, by the following table. It is significant that these experimental data reveal no significant deviations from the ordinary distribution laws, which indicates that there is virtually no thermal decomposition, or other interfering reaction, under the conditions of the experiments. The data presented in the table also illustrate the amount of adsorbing liquid which should be used, in the separation of the metal carbonyl from carbon monoxide by counter-current scrubbing. The latter operation is generally conducted at a temperature below 25° C. (preferably below 10° C.), under a pressure of about 1 to 5 atmospheres.

TABLE II

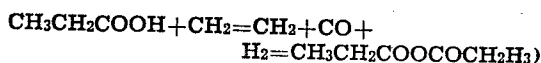
Distribution of nickel carbonyl between carbon monoxide gas and liquid propionic acid at atmospheric pressure

Temperature, °C.	Mol Fraction of Ni (CO) ₄ in Vapor Phase	Mol Fraction of Ni (CO) ₄ in Liquid Phase
-10	.00105	.061505
-10	.0115	.0151
-10	.05	.063
0	.00185	.001505
0	.0182	.01505
0	.073	.063
10	.0031	.0015
10	.0266	.0151
10	.1005	.063
25	.0064	.0015
25	.051	.0151
25	.165	.063
50	.122	.0151
50	.32	.063
80	.29	.0151
80	.64	.063

The invention is illustrated further by means of the following examples.

Example 1.—A mixture of 20 grams nickel propionate and 100 cc. of propionic acid are charged into a pressure-resistant copper-lined reaction vessel, and hydrogen is injected into the mixture until the pressure reaches 50 atmospheres. Into the resulting mixture carbon monoxide is injected and the mixture is heated until the total pressure reaches 200 atmospheres at 200° C. The mol ratio of H₂:Ni in the reaction mixture is initially about 7:1, and the mol ratio of CO:H₂ is 1.35:1. The mixture is heated for 0.5 hour at 200° C., after which the resulting product, which is rich in nickel carbonyl, is cooled, withdrawn from the reaction vessel, and analyzed. The analysis shows that all but 0.075 gram of the Ni has been converted to nickel carbonyl. The experiment is repeated using successively smaller initial quantities of hydrogen, without a substantial decrease in the conversion of nickel propionate to nickel carbonyl until the initial mol ratio of H₂:Ni approaches 1:1, but at H₂:Ni ratios below 1:1 the conversion to nickel carbonyl drops off gradually, and is virtually zero when no hydrogen at all is initially present.

Example 2.—A solution of nickel propionate in propionic acid (0.029 mols of nickel propionate per mol of propionic acid) is pumped through a reaction vessel along with carbon monoxide, ethylene and hydrogen (relative quantities of reactants: 2.5 pounds of propionic acid solution per 32 cubic feet carbon monoxide, 32 cubic feet ethylene and 0.6 cubic feet of hydrogen, S. T. P.) at 275° C., under a pressure of 300 atmospheres, reaction time being 10 minutes. The reaction product containing propionic anhydride (formed by the reaction



is continuously withdrawn and the pressure is let down to about 1 atmosphere. The gas phase in the resulting mixture contains about 0.2% by volume of nickel carbonyl. The liquid phase is withdrawn, and is passed at a temperature of 30° C., through a packed stripping column counter-current to a stream of carbon monoxide at about atmospheric pressure, whereby nickel carbonyl is removed from the liquid phase until only 1.45% of the nickel originally charged remains therein. The gas phase is then conducted to an absorber where it comes in contact with a counterflowing stream of propionic acid at about atmospheric pressure at a temperature of 0° C. The liquid effluent from this absorber provides a solution of catalyst suitable for use in the propionic anhydride synthesis step.

It is to be understood that the above examples are illustrative only and that many different embodiments of the invention will occur to those who are skilled in the art. The invention is, of course, not limited to the use of nickel propionate as the metal salt, since other nickel or cobalt salts of organic carboxylic acids may be employed, e. g. nickel or cobalt acetate, butyrate, benzoate, stearate, naphthenate, etc.

The reaction vessel employed in the practice of the invention may be made of or lined with any reasonably inert material such as inert metals, glass, porcelain, or the like. The reaction may be conducted either batchwise or continuously. Hydrogen may be produced in situ from hydrogen donors, but generally this is neither necessary nor desirable. In view of the foregoing, it will be understood that the invention is not limited except as set forth in the following claims.

We claim:

1. The method for the synthesis of carbonyls of metals of the class consisting of nickel and cobalt which comprises simultaneously interacting an organic carboxylate of the said metal with carbon monoxide and hydrogen and thereafter separating from the resulting mixture the metal carbonyl produced by the said interaction.

2. In a process for the synthesis of metal carbonyls the step which consists in forming a metal carbonyl of the class consisting of nickel carbonyl and cobalt carbonyl by reacting a metal salt of an organic carboxylic acid, said metal being a member of the class consisting of nickel and cobalt, with carbon monoxide and hydrogen at a pressure of 50 to 3000 atmospheres and a temperature of 100° to 375° C. in the presence of an organic solvent for the said metal carbonyl.

3. The process of claim 2 in which the mol ratio of H₂:Ni in the reaction mixture is from 0.1:1 to 5:1 and the mol ratio of CO:H₂ is not less than 1:1.

4. The process of claim 2 in which the said salt is nickel acetate.

5. The process of claim 2 in which the said nickel salt is nickel propionate.

6. The process of claim 2 in which the said nickel salt is nickel naphthenate.

7. The process of claim 2 in which the organic solvent is a normally liquid aliphatic carboxylic acid.

8. A process for the synthesis of nickel carbonyl 10 which consists in reacting nickel propionate, in a propionic acid solvent, with hydrogen and carbon monoxide at 175° to 320° C. under a carbon monoxide partial pressure of 100 to 1000 atmospheres, the initial mol ratio of H₂:Ni being from 1:1 to 2:1, and the initial mol ratio of CO:H₂ being from 25:1 to 500:1, whereby a propionic acid solution of nickel carbonyl is obtained.

9. A process for synthesis of nickel carbonyl 20 and recovery of nickel-containing catalysts which comprises introducing into a reaction vessel a mixture of ethylene, carbon monoxide, propionic acid, a catalytic quantity of nickel propionate, and a quantity of hydrogen such that the mol ratio of H₂ to total Ni is from 1:1 to 2:1, heating 25

the said mixture at a temperature within the range of 175° to 375° C. under a pressure of 100 to 1000 atmospheres, whereby a product containing propionic anhydride and nickel carbonyl is produced, lowering the pressure on the said product until a pressure within the range of 1 to 5 atmospheres is reached, separating a liquid phase from the gas phase in the resulting mixture, contacting the said liquid with a countercurrently flowing stream of carbon monoxide at a pressure of from 1 to 5 atmospheres, at a temperature of 50° to 100° C., whereby the nickel carbonyl is removed from the liquid phase, conducting the said stream of carbon monoxide, after it has been in contact 15 with the said liquid, into an absorber where it comes in contact with a countercurrently flowing stream of liquid propionic acid at a temperature not greater than 25° C., whereby a solution of nickel carbonyl in propionic acid is obtained.

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No references cited.