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PROCESS FOR FORMING COBALT HYDROCARBONYL

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The present invention relates to a process for forming cobalt hydrocarbonyl, and more particularly to a process for forming cobalt hydrocarbonyl in high yield.

Cobalt hydrocarbonyl $HCo(CO)_4$ is a useful hydrogenation catalyst. It has been postulated that the intermediate catalytic step in the oxo synthesis comprises the interaction between cobalt hydrocarbonyl and the olefin used in the oxo synthesis. The properties of cobalt hydrocarbonyl have been reported in literature. Thus, cobalt hydrocarbonyl is a white to pale yellow crystal which melts at about —33° C. and is extremely sensitive to air and water. Cobalt hydrocarbonyl decomposes relatively rapidly at temperatures above —33° C. to dicobalt octacarbonyl.

Prior synthetic methods for forming cobalt hydrocarbonyl have been in the main incapable of achieving satisfactory yields. For example, earlier researches in which cobalt hydrocarbonyl was synthesized by the reaction of carbon monoxide and hydrogen on dicobalt octacarbonyl produced the cobalt hydrocarbonyl in yields generally within the range of one to three percent.

This invention has as an object the provision of a method for producing cobalt hydrocarbonyl in relatively high yields, such as in yields of the order of seventy percent.

Other objects will appear hereinafter.

The process of the present invention for forming cobalt hydrocarbonyl comprises contacting in a confined vessel at a temperature of at least 75° F. (room temperature) and at a super-atmospheric pressure, and preferably a relatively high pressure, such as a pressure greatly in excess of fifty atmospheres, a mixtures comprising cobalt octacarbonyl, hydrogen and carbon monoxide, cooling the pressurized mixture to a temperature at least as low as —33° C., and depressurizing the cooled mixture.

It is most desirable that the process of the present invention be effected in the absence of any olefinic compounds, and preferably in the presence of an excess of hydrogen. It is preferred that a temperature above room temperature be utilized, and most preferably a temperature somewhat above 100° C. such as a temperature of 110° C. In the preferred embodiment, the reaction vessel is brought to an initial pressure of about one thousand pounds per square inch with CO and after initial heating hydrogen is admitted for a final pressure of about three thousand pounds per square inch or more, giving the desired ratio of H_2/CO.

While the reaction appears to be theoretically between the hydrogen and the octacarbonyl without CO entering into the reduction, the presence of the CO is necessary to keep the cobalt carbonyl complex stable against decomposition so that the stabilized octacarbonyl is available to its full extent for reduction by the hydrogen.

It has been found to be essential, if high yields of the cobalt hydrocarbonyl are to be obtained, that after the reaction between hydrogen and dicobalt octacarbonyl in the presence of carbon monoxide, the pressurized mixture be cooled in the presence of the gases to a temperature of at least as low as —33° C., with the depressurizing of the cooled mixture being effected only after the cooled mixture has attained such low temperature. Thus, it has been found that when the mixture of reactants and cobalt hydrocarbonyl product is first depressurized and then cooled, the low yields reported in the prior art, such as yields of one to three percent, are obtained.

The process of the present invention permits the aforesaid relatively high yields to be obtained with relatively low times of reaction. For example, Hieber et al. in Z. Anorg. Chem., volume 240, page 261 (1939), described a typical low yield prior art process in which a reaction time of eighteen hours and a reaction temperature of 165° C. was utilized. In contrast, in applicant's high yield process relatively short reaction times, such as reaction times of the order of somewhat more than one hour and relatively low reaction temperatures, such as heretofore indicated may be utilized.

By way of example there is set forth below a typical run which illustrates the process of the present invention:

Example

0.78 gram of dicobalt octacarbonyl disposed in 100 milliliters of hexane were added to an autoclave having a 250 milliliter capacity. The autoclave was pressurized with carbon monoxide to a pressure of 85 atmospheres. The autoclave was then heated with agitation to a temperature of 110° C. for seventy minutes at which time the internal pressure was 110 atmospheres. Hydrogen was then added to the autoclave until a molar ratio of hydrogen to carbon monoxide of two to one was obtained. Under these conditions the total pressure within the autoclave was 220 atmospheres. Heating of the autoclave was then terminated, and the autoclave was permitted to cool to room temperature. Upon attaining room temperature, the autoclave was then cooled to —70° C., and after the pressure ceased dropping the gases within the autoclave were vented and the autoclave opened. Under the aforesaid conditions a total yield of 70% of cobalt hydrocarbonyl was obtained.

The reaction product can be used as such in catalyzing hydrogenation reactions, oxo reactions, $CO+H_2$ synthesis, etc. The high concentration of active catalyst, $HCo(CO)_4$, makes such a mixture quite effective. However, if more concentrated or essentially pure cobalt hydrocarbonyl is desired, the differences in physical (vapor pressure) characteristics between the monomeric hydrocarbonyl and dimeric octacarbonyl permit a facile separation at low temperatures by vacuum distillation, preferably in a stream of carbon monoxide. Because of the extremely sensitive stability of the hydrocarbonyl it is necessary to distill at —33° C. or thereabout and at reduced pressure, preferably with carbon monoxide as a carrier gas, to avoid dissociation. Thus, at —30° C. and 15 mm. Hg pressure, the gaseous distillation product would comprise 66 vol. percent of carbon monoxide, 33 vol. percent of cobalt hydrocarbonyl and less than 1 vol. percent of cobalt octacarbonyl.

It is to be noted that in the process of the present invention rapid cooling of the autoclave to a temperature of below —33° C. is not necessary. Thus, the autoclave may be cooled in stages, as in the example, wherein it was first cooled to room temperature and then to a temperature below —33° C. It is essential in all cases that the cooling to a temperature at least as low as —33° C. be accomplished prior to the venting of gases from the autoclave.

The H_2/CO ratio in the reaction vessel at the start of the reaction should not be below 1/4 and may be as high as 4/1, the preferred range lying between 1/2 and 2/1.

The hydrogen should be present in an amount in excess of that theoretically demanded by the reaction.

$$[Co(CO)_4]_2+H_2\rightarrow 2HCo(CO)_4$$

The present invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof, and accordingly, reference should be made to the appended claims, rather than to the foregoing specification as indicating the scope of the invention.

It is claimed:

1. A process for forming cobalt hydrocarbonyl as the principal reaction product, which comprises contacting at a temperature of at least 75° F. and at a super-atmospheric pressure a mixture composed of dicobalt octacarbonyl, hydrogen, and carbon monoxide, the molar ratio of hydrogen to carbon monoxide being in the range of 1/4 to 4/1; cooling the pressurized mixture to a temperature at least as low as —33° C., and depressurizing the cooled mixture.

2. A process for forming cobalt hydrocarbonyl as the principal reaction product, which comprises contacting in a confined vessel at a temperature of at least 75° F. and at a super-atmospheric pressure a mixture composed of dicobalt octacarbonyl, hydrogen, and carbon monoxide, the molar ratio of hydrogen to carbon monoxide being in the range of 1/4 to 4/1; cooling the pressurized mixture to a temperature at least as low as —33° C., and depressurizing the cooled mixture.

3. A process for forming cobalt hydrocarbonyl which comprises contacting in a confined vessel at a temperature of at least 212° F. and a pressure in excess of one thousand pounds per square inch an olefin-free mixture comprising dicobalt octacarbonyl, hydrogen, and carbon monoxide, the molar ratio of hydrogen to carbon monoxide being in the range of 1/4 to 4/1; cooling the pressurized mixture to a temperature at least as low as —33° C., and depressurizing the cooled mixture.

4. A process in accordance with claim 3 in which the H_2/CO ratio of the mixture initially present in said confined vessel lies in the range of 1/2 to 2/1.

5. A process for forming cobalt hydrocarbonyl as the principal reaction product, which comprises contacting in a confined vessel at a temperature of about 110° C. and at a maximum pressure of about 220 atmospheres a mixture composed of dicobalt octacarbonyl, hydrogen, and carbon monoxide, with the molar ratio between the hydrogen and carbon monoxide being about two to one, cooling the pressurized mixture to a temperature below —33° C., and depressurizing the cooled mixture.

References Cited in the file of this patent

UNITED STATES PATENTS

2,477,553	McKeever	July 26, 1949
2,747,986	Gwynn	May 29, 1956
2,767,048	Mertzweiller	Oct. 16, 1956

OTHER REFERENCES

"The Volatile Metal Carbonyls," by A. A. Blanchard. Publ. in Chemical Reviews, vol. 21, 1937, page 4.

The Chemistry of Metal Carbonyls. Preparation and Properties of Cobalt Hydrocarbonyl, by H. W. Sternberg et al. Publ. in the Journal of the American Chemical Society, vol. 75, 1953, page 2717.

P. Pino et al.: Chimicae Industria (Milan), vol. 37, pp. 782–6 (1955).

M. Orchin, L. Kirch and I. Goldfarb: Journal of the American Chemical Society, vol. 78, 1956, pp. 5450–5451.