Patented June 16, 1953

2,642,356

UNITED STATES PATENT OFFICE

2,642,356

LOW-TEMPERATURE REDUCTION OF NICKEL CHLORIDE

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No Drawing. Application May 23, 1950, Serial No. 163,791

4 Claims. (Cl. 75—0.5)

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The present invention relates to the low temperature reduction of nickel chloride and more particularly to the reduction of nickel chloride to form finely divided metallic nickel at temperatures below that at which this material could be reduced in the absence of a catalyst in accordance with previously known methods.

For many purposes it is desired to prepare nickel in a very finely divided condition. Such material may, for example, find a use as a catalyst in numerous hydrogenation reactions, wherein the value of a material as a catalyst is to a certain extent at least enhanced by a finer state of subdivision. Finely divided nickel is also useful in powder metallurgy, particularly where the nickel is to be mixed with some other powdered metal, for example iron, in making composite articles. When the nickel used is in a very finely divided condition, the resulting articles made by powder metallurgy processes are much more homogeneous than if the nickel were used in the form of coarser particles. In some instances also the fineness of the nickel powder may make for greater strength in a product made therefrom.

It is known that nickel powder formed by chemically reducing a compound of nickel is smaller in particle size substantially in proportion as the temperature at which the reduction takes place is lower. For this reason, it has been desired, when finely divided nickel is the desired product, to effect the reduction at as low a temperature or temperature range as possible. Prior art practices and certain tests hereinafter set out in the examples given demonstrate that at temperatures below about 650° F. the reduction to nickel from one of its salts, for example, from nickel chloride, proceeds at such an extremely slow rate that it may be said for practical purposes, that it is impossible to reduce nickel chloride below this temperature in the absence of some catalyst which will enable the reaction to take place at an appreciable rate in the desired lower temperature range.

The present invention may be summarized therefore as one providing a process for the preparation of finely divided metallic nickel from a salt of nickel, for example, nickel chloride, in a temperature range of about 475° F. to about 650° F. In this range it is found that the reduction reaction will take place if it is catalyzed by the presence in the mass to be reduced of a desired catalyst, namely, finely divided metallic nickel, the product of the reduction reaction. Inasmuch as the catalyst is itself the product of the reaction being catalyzed, it may be said that the

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process is autocatalytic, that is, it will proceed at a practical rate once it is initiated by the presence of at least a trace, or a so-called "threshold amount" of the catalyst.

It is further found that the rate of such reduction is enhanced by greater amounts of the catalyst and also, independently, by increased temperatures in the range at which the reduction reaction takes place. It has been found, for example, that at temperatures above about 650° F. the reaction will go on even without a catalyst to initiate it, even though the reduced material at these higher temperatures is in much larger particle size than is desired in accordance with the present invention.

While it is contemplated, and it has been proven as hereinafter set forth, that a trace, or a so-called threshold amount only of the catalyst (i. e., finely divided metallic nickel) will be sufficient to initiate the reduction reaction, it is believed that, from a practical standpoint, at least about 0.1% of metallic nickel (calculated by weight based upon the weight of the nickel chloride to be reduced) is required in order to start the reduction reaction at any appreciable and economical practicable rate. For this reason the minimum amount of metallic nickel normally usable in initiating the reduction of the nickel chloride may be said for purposes of this invention to be about 0.1%, calculated as aforesaid.

In view of the fact that larger amounts of the catalyst will cause the reaction to occur with greater rapidity even at a given temperature, it is useful to employ larger amounts of the catalyst than the minimum above referred to. This causes no substantial loss, as the product itself is the catalyst and, therefore, a portion thereof may be returned from one batch to a succeeding batch in the practical working of the process. In this way the only loss in the repeated practice of the process is the heat that is required to reheat a certain amount of the catalyst, i. e., the product of an earlier batch. Corresponding economies may be effected on a continuous basis of operation. The process as a whole, which is carried on at a substantially lower temperature than was heretofore deemed possible, will save a much larger total amount of heat than that lost as aforesaid and hence is more economical.

The process of the present invention is best illustrated by the following examples:

Example I

About 10 grams of anhydrous nickel chloride was placed into each of two similar porcelain

boats, which were simultaneously exposed side by side in a furnace through which hydrogen gas was passed substantially continuously, the boats and the furnace being maintained at a temperature of about 500° F. In one of these two samples about 16% finely divided metallic nickel was added to and thoroughly mixed with the nickel chloride prior to the placing of this mixed material in the furnace; while in the other no metallic nickel was intentionally placed. The material was maintained in the furnace at the temperature aforesaid and exposed to a continuous flowing stream of hydrogen for a period of about 35 hours. At the end of this time the contents of the two porcelain boats were cooled, removed and analyzed. The sample consisting of a nickel chloride mixed with metallic nickel was found to have been substantially completely reduced, actual analysis of the content of this sample, showing 99.3% metallic nickel. The contents of the other boat, to which no metallic nickel was intentionally added, was found to be almost completely unreduced. The only metallic nickel found in this second boat was at a pinpoint location in the sample and indicated that a particle of metallic nickel was probably accidentally transferred to this point in the second sample by entrainment in the gas stream. Immediately around this pinpoint area there was a spot about $\frac{1}{16}$'' in diameter where the nickel chloride had been reduced to metallic nickel. The remainder of the sample was completely unreduced.

Example II

Hydrated nickel chloride ($NiCl_2.2H_2O$) was first dehydrated in a stream of nitrogen at about 700° F., then cooled to about 600° F. and the nitrogen atmosphere exchanged for a hydrogen atmosphere which was caused to flow continuously past the sample for about 6 hours. Careful check was made of the outgoing or exhaust gas to determine the presence af any HCl therein which would result from reduction of the material of the sample by the hydrogen. There was no reduction perceptible by this test in the time permitted as aforesaid. When, however, without other change, the temperature was raised to the range of about 650° F. to about 700° F., perceptible reduction started as was evidenced by the presence of HCl in the exit gas.

Example III

The same test as in Example II was made with the exception that the hydrated nickel chloride was not first dehydrated prior to being exposed at the reducing conditions stated in Example II in the hydrogen atmosphere. The results were identical with those given in Example II.

Example IV

A sample of anhydrous nickel chloride to which about 16% of its weight of finely divided metallic nickel was added and thoroughly admixed was exposed as in Examples II and III to a flow of hydrogen, first at about 450° F. At this temperature, there was no discernible reduction taking place as evidenced by the fact that no HCl was found in the exit gas. Upon the temperature being raised to about 475° F. the exit gases began to show some HCl content. As the temperature was progressively raised in about 10° steps, the HCl content in the gases was progressively greater, indicating a progressively increased rate of reduction as the temperature was raised.

Example V

The same test as in Example IV was made, using nickel chloride dihydrate in lieu of anhydrous nickel chloride. The results were exactly the same as in Example IV above.

It has been found that in order to reduce nickel chloride to metallic nickel, the gaseous reducing agent must contain hydrogen, as hydrogen is the only gas which has been found, in accordance with the present invention, to be effective in reducing nickel chloride to metallic nickel. It seems immaterial what the proportion of the hydrogen is in the gases or what other gases may be present, assuming, that is, that the other gases are not positively oxidizing or chloridizing in character. These other gases are preferably substantially neutral in character, such as nitrogen, for example. For this reason hydrogen is considered, in accordance with the present invention, to be the essential active reducing ingredient of the gas to which the nickel chloride is exposed in order to effect the reduction thereof.

From the above it will be noted that one way of practicing the process of the present invention is to mix with nickel chloride, with or without water of crystallization, a desired amount of finely divided metallic nickel as a catalyst to initiate the reducing reaction in the low temperature range. Another way of attaining the same results is, of course, in any way to provide in the mass of nickel chloride to be reduced, the desired catalyst. As it has been found, as above set forth, that the reduction will take place in the absence of a catalyst at higher temperatures, this high temperature reduction may sometimes be resorted to to form or to establish in the mass, the desired amount of metallic nickel to act as the catalyst. Following the establishment of the initial desired amount, the temperature may be lowered to a point or range within the desired range in accordance with the present invention, i. e., from about 475° F. to about 650° F., and then the process of the present invention carried on. The present process is to be considered to include such practice.

While there is herein described but one principal process and certain variants thereof, the present invention is intended to include all reasonable equivalents of the steps specifically set out herein, as will occur to those skilled in the art from the foregoing disclosure.

What is claimed is:

1. The process of initiating the reduction of solid nickel chloride ($NiCl_2$) with hydrogen by a dry gas-to-solid reaction to form metallic nickel in a temperature range in which hydrogen and $NiCl_2$ will not commence to react together to any substantial extent in the absence of a reaction-initiating catalyst, comprising the steps of contacting dry solid $NiCl_2$, which is substantially free of metallic nickel, with a gas containing hydrogen as its essential active reducing ingredient, while maintaining said $NiCl_2$ in the temperature range of about 475° F. to about 650° F., and causing the reaction to start by providing in contact with the $NiCl_2$ at least about 0.1% (by weight based upon the $NiCl_2$) of metallic nickel as a reaction-initiating catalyst.

2. The process according to claim 1, wherein said gas consists of hydrogen.

3. The process according to claim 1, wherein there is provided in contact with said nickel chloride about 16% of finely divided metallic nickel for initiating the reduction of said nickel chloride.

4. The process according to claim 1, in which

said metallic nickel for use as a reaction-initiating catalyst is provided by forming such metallic nickel in situ by reducing some $NiCl_2$ at a temperature above 650° F.

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