

UNITED STATES PATENT OFFICE.

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METHOD OF MAKING CATALYSTS.

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Specification of Letters Patent.

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No Drawing.

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To all whom it may concern:

Be it known that I, WALTER O. SNELLING, a citizen of the United States, residing at Pittsburgh, in the county of Allegheny and State of Pennsylvania, have invented certain new and useful Improvements in Methods of Making Catalysts, of which the following is a specification.

This invention relates to methods of making catalysts; and it comprises a process of making highly reactive catalytic metals, either as metallic powders, or embodied in or on a carrier such as a porous material such as pumice stone, kieselguhr, petroleum coke, clay, etc., wherein a formate of a catalytic metal, such as copper, nickel, cobalt, or iron, is reduced by direct heating in a dry state at low temperatures; all as more fully hereinafter set forth and as claimed.

Catalytic metals are now largely employed in a number of arts, as in the hardening of oils by hydrogen in the presence of nickel, the formation of formaldehyde from methyl alcohol and air in the presence of copper, etc. For all these uses, the physical condition of the metal is of great importance, since upon this condition depends its chemical activity; and this condition in turn depends upon the circumstances under which reduction is performed, that is under which the metal is formed. Nickel, for example, when reduced from the oxid by hydrogen at 300° is in a different state and is more active than when reduced at 350°. For a maximum activity, the metal should be reduced at the lowest possible temperature and should be, as nearly as possible, in an almost molecular state of fineness. Any sintering or welding reduces the activity enormously; which is probably one of the reasons why low temperature reduction is advantageous. Ordinarily, the nitrates of the metals are taken and these converted into oxids by roasting and then the oxid is reduced in a tube at a low temperature by hydrogen. For many purposes neither the chlorids nor the sulfates can be used. If the oxid is used without a carrier, this reduction operation results in the formation of a velvety powder of extreme fineness, usually pyrophoric on exposure to air. Very often a carrier, such as porous clay, kieselguhr, pumice stone, etc., is employed; the carrier being soaked in a solution of the nitrate and then roasted and reduced. In this oper-

ation the heating must be, relatively, high to cause reduction throughout the body of the particle of carrier.

Whether or no a carrier be employed, it is difficult in this operation to secure a good reduction at a very low temperature and obtain as highly reactive catalysts as are desirable and especially when operating with any substantial amount of material. Heat transmission through either a powder or a porous material is slow; and at comparatively low temperatures the reducing power of gaseous, that is molecular, hydrogen is also slow. But to work with any speed it is necessary to have a high temperature to force the heat through the slowly conducting material. And in the use of a siliceous carrier with an oxid it is difficult to prevent more or less formation of slaggy compounds.

I have found that an article of high reactivity can be prepared by suitably heating the metallic formates, the reduction of the formates taking place at a very low temperature, and proceeding smoothly. Nickel formate, cobalt formate, iron formate, copper formate, etc. may be used; and the formates may be used in the dry state where a powder is required; or a porous carrier may be soaked with a solution of the formate, dried and reduced. On heating, the formates tend to break up, empirically speaking, with an evolution of carbon monoxid and hydrogen, both strongly reducing gases; and this evolution of these gases *in statu nascendi*; so to speak, allows the formation of highly reactive metal at very low temperatures. It is not necessary as in the case of nitrates, etc., to supply the reducing means from another source; which is a great advantage in the case of forming the catalyst in a carrier. In the formates, the combustible and the oxygen of the metal oxid are, so to speak, in atomic or molecular contact; a contact differing from that of the oxid as powder in an atmosphere of hydrogen. And as the reduction of the metal oxid and the oxidation of the combustible as a total reaction is exothermic, a reduction change started in one portion of a mass of formate tends to spread through it; the reaction can be initiated at one point and allowed to spread through the material as a self-propagating reaction. And the reduction may be effected at a comparatively very low temperature; a temperature at which there is no tendency of the reduced metal to sinter

or of the oxids to slag. After reduction is complete the temperature is of course not raised; the heating ends at the lowest temperature at which reduction to metal will take place.

5 I shall more particularly speak hereinafter of the formation of reactive copper; but the present invention is applicable to the formation of other catalytic metals, such as nickel, cobalt, iron, palladium, etc.

10 In making reactive copper where the metal is desired in pulverulent form, the copper formate after first drying at a low temperature may be placed in a tube or other 15 container and cautiously heated to the lowest temperature at which the formation of metal becomes evident. The air in the tube is best displaced by hydrogen or the like prior to the heating. The formate may be 20 dried in the container in which reduction is subsequently to be effected. In so doing it is advantageous to pass through a stream of hydrogen or other non-oxidizing gas. This stream carries away as fast as formed 25 the water produced in drying and that produced in the subsequent reduction and much facilitates both operations. Vacuum may be used in lieu of hydrogen. Where the copper 30 is desired on a carrier, as is usually the case, the carrier may be soaked in a solution of copper formate, and the impregnated material dried and heated in the same way. It is particularly advantageous in this case after placing the impregnated carrier in the reduction vessel to produce a vacuum to get 35 rid of absorbed and adsorbed air. Hydrogen may then be allowed to enter and the material heated.

40 The porous carrier employed may be any of the usual refractory materials. For nickel, cobalt, iron, copper, etc. where used for hydrogen addition, as in hardening fats and the like, the carrier may be coke. Where used in oxidizing reactions, as in the 45 manufacture of formaldehyde the carrier is better an inoxidizable material such as pumice-stone, baked clay, kieselguhr, etc. For many purposes I find that "alundum" (a commercial form of fused alumina) is a 50 very desirable carrier since in many reactions alumina has a tendency to act as a co-catalytic. It is particularly advantageous in making a copper catalyst for the manufacture of formaldehyde.

55 The amount of catalyst used with the porous carrier can of course be as may be desired for the particular purpose in view. A carrier can be impregnated with any desired proportion of catalyst by using a 60 formate solution of predetermined strength. The formates being of low molecular weight and quite crystalline, their solutions diffuse readily and it is therefore easy to secure good impregnation. For many purposes in 65 catalytic operations it is desirable to have a

column of catalytic material wherein the carrier has different proportions of catalyst embodied in it at different points throughout the column. For example, in making formaldehyde from methyl alcohol and air 70 it is advantageous to have the mixed vapor and air pass first through an "alundum" carrier containing a relatively small amount of copper, then past a carrier containing more, and so on until the mixture finally 75 passes a carrier relatively rich in catalyst. It is, so to speak, advantageous to have the concentration of catalyst and the concentration of the reactive bodies inversely proportional in any given zone of catalysis. 80 Similarly in hydrogenation processes involving the addition of hydrogen to vapors and gases, it is advantageous to have the gas mixture first pass through a carrier containing relatively little reduced nickel and 85 subsequently past a carrier containing more nickel. These catalytic reactions are apt to be, relatively, violent in their first inception and slow down afterward (thermal conditions being alike) and for this reason it is 90 better to have the reaction begin in the presence of a relatively small amount of catalyst and continue in the presence of more.

95 The reduction of the formate should be at the lowest possible temperature; and the material should be brought to this temperature rather gradually. Careful observation of any given formate will show to the eye the point where reduction begins. Any sudden or violent heating causes a sudden decomposition of the formate with the liberation of CO and H₂ in the gaseous form; after which reduction can only be in the ordinary way; viz. by a reducing atmosphere. And with violent heating the reaction, 100 under the catalytic influence of the metal, is apt to be irregular and result in the production of carbon and other, more or less, indefinite bodies.

105 What I claim is:

1. In the manufacture of a catalyst, the process which comprises heating a dry metallic formate to the lowest temperature at which reduction takes place.
2. In the manufacture of a catalyst, the process which comprises heating dry copper formate to the lowest temperature at which reduction takes place.
3. In the manufacture of a catalyst, the process which comprises heating a metallic 120 formate in an atmosphere of hydrogen to the lowest temperature at which reduction takes place.
4. In the manufacture of a catalyst, the process which comprises heating copper 125 formate in an atmosphere of hydrogen to the lowest temperature at which reduction takes place.
5. In the manufacture of a catalyst, the process which comprises impregnating a 130

porous carrier with a solution of a metallic formate and heating.

6. In the manufacture of a catalyst, the process which comprises impregnating a porous carrier with a solution of copper formate and heating.

7. In the manufacture of a catalyst, the process which comprises heating a dry metallic formate in an atmosphere of inert gas, to the lowest temperature at which the desired reduction will take place.

8. In the manufacture of a catalyst, the process which comprises heating dry copper formate in an atmosphere of inert gas, to the lowest temperature at which the desired reduction will take place.

9. In the manufacture of a catalyst, the process which comprises heating a metal

formate while removing moisture as fast as evolved or formed, such heating ending at 20 the lowest temperature at which reduction to metal will take place.

10. In the manufacture of a catalyst, the process which comprises heating copper formate while removing moisture as fast as 25 evolved or formed, such heating ending at the lowest temperature at which reduction to metal will take place.

In testimony whereof, I affix my signature in the presence of two subscribing witnesses.

WALTER O. SNELLING.

Witnesses:

K. P. McELROY,
H. SCHOENTHAL.