

THE HYDROGENATION OF CARBON DIOXIDE UNDER PRESSURE

IN THE PRESENCE OF

SEVERAL METALLIC CATALYSTS

by

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B. S. Illinois Wesleyan University, 1925

A THESIS

submitted in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

KANSAS STATE AGRICULTURAL COLLEGE

1929

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INTRODUCTION

There has been, of late, both a widespread and a popular interest in an extremely fascinating and comparatively slightly understood phenomenon called, for want of a better term, catalysis.

History

This phenomenon, although at the present time employed extensively in industries ranging from solid fat production from vegetable oils like cottonseed oil, to the manufacture of acetic acid from acetylene gas, reaches far back into history. For the ancients used catalysts (enzymes which they called "ferments") in converting fruit juices into wines. Moreover, the Arabians(1) are credited with the discovery of the catalytic process for making diethyl ether from alcohol by the use of sulfuric acid.

In 1794 Mrs. Fulhame of London in a paper(2) on combustion pointed out the necessity of traces of water in order to bring about the union of carbon monoxide with oxygen.

(1) Rideal and Taylor: Catalysis in Theory and Practice, page 3. Macmillan and Co. 1919.

(2) Fulhame: An Essay on Combustion. London. 1794.

Kirchof(3) in 1811 appears to have made the first scientific observation of a catalytic transformation by showing that mineral acids, in hot water solution, although themselves unaltered in the presence of starch, still change the starch into dextrin and sugar. Sir Humphrey Davy(4) in 1817 observed the ability of a slightly heated platinum spiral to bring about the oxidation of hydrogen, carbon monoxide, or hydrocyanic acid. Henry(5), in an article published in 1825, noted that at 170 degrees "carbonic oxide" and hydrogen when mixed with each other in equal volumes and oxygen added sufficient to react with only one of them, in the presence of a platinum catalyst, reacted in the ratio of four to one; that is four-fifths of the oxygen combined with the "carbonic oxide" and only one-fifth with the hydrogen. Dobereiner about this time was working on the combustion of hydrogen and oxygen mixtures in the presence of a cold platinum catalyst. Berzelius, in his "Treatise on Chemistry"(6), discussed catalytic phenomena and named them in general, "catalytic", from the Greek words meaning

(3) Sabatier: Catalysis in Organic Chemistry, translated by E. Emmet Reid, page 1. Van Nostrand and Co. 1923.

(4) Same as (3).

(5) Phil. Mag.: 65;269. 1825.

(6) Berzelius: Traite de Chemie: I; 110. 1845.

"down" and "I unloose". Faraday(7) made a detailed inquiry into "the power of metals and other solids to induce combination of gaseous bodies". Other investigators published data at various times between this and the year 1897, when Sabatier began his investigations in organic chemistry.

Attempts to Define Catalysts

The origin of the term "catalyst" has been noted above. Berzelius(8) in 1835 said, in part, "... catalytic power appears to consist essentially in the fact that substances are able to set into activity affinities which are dormant at this particular temperature by their presence alone." Ostwald(9) defined a catalyst as "a substance which change the velocity of a given chemical reaction without modification of the energy factors of the reaction." Sabatier(10) defines catalysis as "the mechanism by virtue of which certain chemical reactions are caused, or accelerated, by substances which do not appear to take any part in the reactions." The view of the "increase in concentration of the reacting component" is brought out in Steiglitz' work.

(7) Phil. Trans.: 114; 55. 1834.

(8) Steele; Physical Chemistry and Biophysics: page 314. Chapman and Hall, London. 1928.

(9) See (1) page 12.

(10) See (3) page 1.

His extensive studies on the rate of hydrolysis of imido esters in the presence of highly ionized acids as catalysts seem to support this theory(11). There has been a statement made(12), "A catalyst modifies the velocities of two inverse reactions to the same degree and therefore cannot affect the final state of equilibrium". Further(12), "A catalytic agent is incapable of starting a reaction; it can only modify the velocity of a reaction already taking place".

Kind of Reactions Subject to Catalytic Action

Chemical reactions may, in general, be divided into two classes, namely, ionic(or instantaneous) and slow. The reactions of the latter type are for the most part catalytic in character(13). Thus catalytic studies are concerned with slow reactions,--ones apparently already taking place to some extent, the object being, of course, to speed up the reactions so that equilibrium conditions are reached in a shorter time.

Classes of Catalysts

Catalysis may be divided into two general classes,

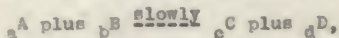
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- (11) Falk: Catalytic Action: pp. 32,35. Chemical Catalogue Co., Inc. 1922.
 - (12) H. S. Taylor: A Treatise on Physical Chemistry; Vol. II, page 913. D. Van Nostrand Co. 1925.
 - (13) See (13) II; 885.

homogeneous and heterogeneous. In the former case, the catalyst and the reacting system are intimately mixed, being all in one phase. In the latter case, the catalyst is present in one phase (usually the solid) and the reacting system in one or more other phases.

Common type substances which may act as catalysts are (14), carriers, contact agents, hydrogen or hydroxyl ions, enzymes, and water.

Concepts of Catalytic Action

There are varying concepts to explain the mechanism of catalytic action. Falk (15) notes that the formation of intermediate compounds appears to offer the most general explanation of the manner in which a catalyst works. Sabatier (16) probably has done the most to develop the concept of intermediate compound formation. In general, the mechanism may be summarized in the following way. In the reaction:



if A ordinarily unites with B slowly, the intervention of the proper catalyst enables the reaction to proceed more

(14) Noyes and Sherrill: Chemical Principles: 140-143. MacMillan Co. 1926.

(15) See (11) 38 and following.

(16) See (3) page 48.

rapidly in the following way:

A plus catalyst ~~readily~~ Catalyst-A (intermediate compound),
Catalyst-A plus B ~~readily~~ A-B plus catalyst.

This formation of intermediate compounds is used to explain the catalytic action of carriers.

The mechanism of the action of contact agents(17) in catalysis is little understood, but several explanations are advanced. They may be substances in the surface layer of which gases are adsorbed either in the gaseous or liquid state in such concentration that the reaction between them will be accelerated. It may be that the particular catalyst has in its surface, structures which hold reacting molecules in their most vulnerable positions. Another viewpoint is that intermediate compounds are formed on the surface of the catalyst. Still another idea is that contact agents are active only in spots on their surfaces, and that these spots may perhaps hold reacting molecules in more or less a stretched condition(18) so that this distortion or strain will allow them to break at unexpected points when other reacting molecules strike them.

(17) See (14) page 142.

(18) Taylor, H. S.: Journal of Physical Chem.: 32: 1621. 1928. Also Report of Committee on Contact Catalysis: Same journal: 1601 and following.

A familiar example of the catalytic activity of either hydrogen or hydroxyl ions is that of the saponification of esters by either an acid or a base. It is most probable that such reactions involve some intermediate compound formation. Perhaps these ions are to be classified only as assisting in intermediate compound formation. Bronsted(19) has pointed out the existence of hydrated ions. These hydrated ions may be increasingly active due to the promoter effect of water present.

The mechanism of enzyme catalysis is still largely a matter of conjecture and that of the catalytic properties of water probably can be traced toward intermediate compound formation.

Autocatalysis involves a state of affairs in which some material produced in the process acts as a promoting or catalyzing material for the desired reaction.

Just as some catalysts speed a reaction toward equilibrium, so others retard the attainment of equilibrium. These substances are termed negative catalysts.

(19) Bronsted, J. N.: Acid and Basic Catalysis: Chemical Reviews: V; 3; 231. 1928.

Free energy has been defined as the driving force of a chemical reaction. A chemical reaction takes place only until equilibrium has been reached. Free energy, then, is a measure of the driving force toward the equilibrium point for a certain temperature and pressure of the reaction concerned. A positive catalyst should be useful, then, if a reaction is possible thermodynamically. However, free energy change values do not tell how fast a possible reaction will take place. Perhaps a reaction barely possible thermodynamically may be so rapid that it will render one more possible and more slow, only incidental. So predictions made from free energy data must be modified, as will be pointed out later by equilibrium constants for the same reaction.

Free Energy Calculations

According to Lewis and Randall(20), the general method of qualitative prediction of the thermodynamic possibility of a reaction is simple. "If we are interested in the course of some chemical reaction at a certain temperature,

(20) Lewis and Randall; Thermodynamics: page 596. McGraw-Hill Book Co. 1923.

and under certain conditions of pressure and composition, we first add algebraically the equations for the free energies of formation of the several substances, and thus obtain the standard change of free energy....."(for the same temperature at which the free energies of formation are used).

If F has a negative sign, then we know that the reaction is thermodynamically possible. Free energy of formation values are calculated as shown by Lewis and Randall(21) from heat capacities of the substances concerned, and from the heat of decomposition of the desired substances.

Thus for a given hypothetical reaction the free energy change can be calculated. These equations, as pointed out by Francis(22), are often unwieldy and may be simplified to very nearly as accurate linear equations(in the case of free energy of formation of hydrocarbons).

Accordingly, various hypothetical reactions were written in this paper, and by use of the approximate simplified equations(23), free energy values were calculated.

(21) See (20) pp. 173-4;102-4.

(22) Francis, Alfred W.: The Free Energies of Some Hydrocarbons. Ind. Eng. Chem. 20: 274. 1928.

(23) See (22) and also in same journal by same author: The Free Energies of Some Alcohols: page 283.

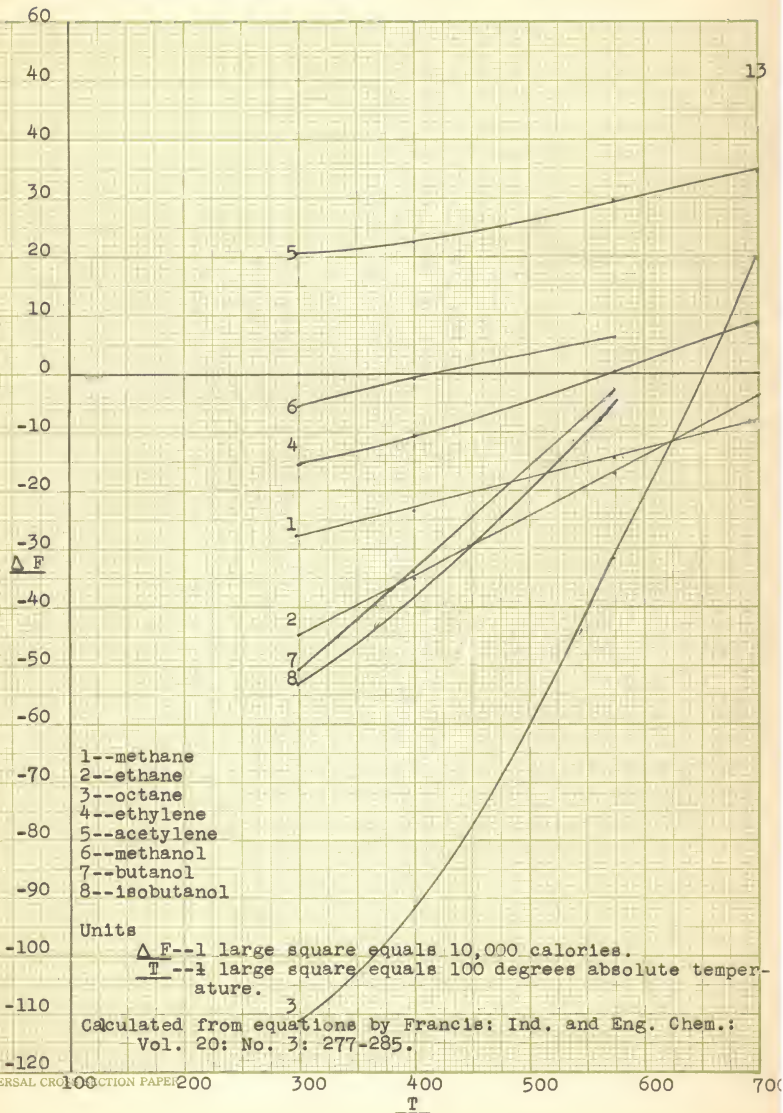
Values so calculated for the free energy change of the formation from carbon dioxide and hydrogen, of the following: methane, ethane, octane, ethylene, acetylene, methanol, butanol, and iso-butanol, are plotted against absolute temperature on Graph I. This graph shows the thermodynamic tendencies, only, of these reactions, without relation to their relative speeds. Graph II, for methane, shows the variation of the equilibrium constant, $\frac{(CH_4)}{(H_2)^4} \frac{(H_2O)^2}{(CO_2)}$, with absolute temperature. This shows quantitatively how much methane should be formed over an active catalyst.

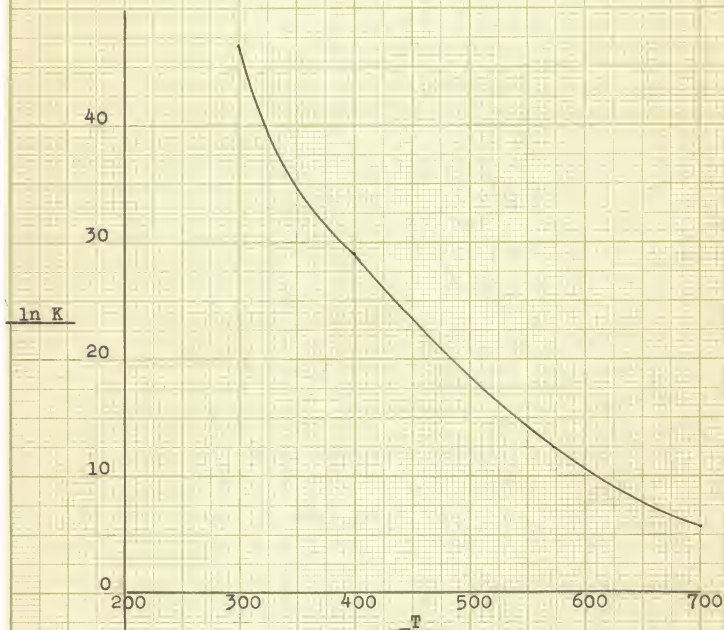
Contact Catalysis

Contact catalysis may take place between gases or solutes in the presence of a solid catalyst. Since at moderate temperatures the reacting substances will usually be gaseous, this type is by far the most common of contact reactions.

Theories attempting to explain the action of contact catalysts include the postulate of preliminary adsorption, or else the formation of an intermediate compound. Perhaps, as the work of Kunsman(22) might indicate, catalytic activ-

(22) Kunsman, as noted by Taylor in Condition of Adsorbed Gases. Journal of Physical Chem.: 32: 928. 1928.





Calculated from $-\Delta F$ equals $RT \ln K$, Noyes and Sherrill:
Chemical Principles: page 241. Macmillan Co. 1926.
Values for ΔF on graph 1 were used.

GRAPH 2
Variation of equilibrium constant for the formation
of methane with temperature

ity of this kind may be related to thermion emission.

At present it seems established that there is not a quantitative correlation(23) between catalytic activity and adsorption. The work done on silica gels has seemed to emphasize this fact. E. S. Taylor(24) states that adsorption is a condition precedent to catalytic change. The recent works(25) include much data on the system, carbon monoxide and hydrogen, in the presence of various catalysts. The work done on the system, carbon dioxide and hydrogen, in the presence of catalysts(26) includes experimental runs made by Fischer, using iron and potassium carbonate as catalyst, and by Maible(27), who has published data on the hydrogenation of carbon monoxide and carbon dioxide over nickel

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- (23) Peirce and Georgin: Journal of Physical Chem.:32: 1423. 1928.
 - (24) Journal of Physical Chem.: 29: 924. 1924.
 - (25) Chemical Abstracts: page 2657; July 20, 1928.
(Synthol) Chemical Abstracts: page 459; 1924.
 - (26) Synthetic Hydrocarbons: Chemical Abstracts: page 1465; 1924.
Synthesis of Higher Hydrocarbons from Water Gas:
Smith, Hawk, and Reynolds: J. Ind. and Eng. Chem.: 20: 1341. 1928.
Lewis and Fer K. Frolich: Synthesis of Methanol from Carbon Monoxide and Hydrogen: J. Ind. and Eng. Chem.: 20: 285. 1928.
 - (27) Chemical Abstracts: page 1465; 1924, or J. Usines Gaz.: 48: 34-37. 1924.

catalysts. Sandall and Girard(28) have recently studied the equilibrium in the formation of methane and water vapor from carbon dioxide and hydrogen over a catalyst. Moreover, Sabatier(29), quite a number of years ago, noted the conversion of hydrogen and carbon dioxide into methane over cobalt catalysts, the inability of copper catalysts to do this,(30), and the great efficiency of catalytic nickel(31) in this conversion.

PURPOSE

The purpose of this problem was to study the effect of nickel and cobalt catalysts prepared in a new way on reactions between carbon dioxide and hydrogen. The usual method of preparing a catalyst is that of precipitation of the metal(or metals) involved as hydroxides, and the subsequent dehydration by heating, followed by reduction of the remaining oxide. In this work, the attempt was made to secure irregular surfaces, catalytic in character, by the rapid electrodeposition of cobalt and nickel upon clean copper spirals.

(28) Sabatier and Senderens: Ann. Chem. Phys.:(8):4:424. 1905.

(29) See (3) 180-181.

(30) See (3) 145.

(31) See (3) 207.

ACKNOWLEDGMENT

The author wishes to express his appreciation for the material help, encouragement, and guidance afforded especially by Dr. H. H. King and Dr. E. B. Keith in the work upon this problem.

MATERIALS USED

The gases used in this experimental work were commercial carbon dioxide and commercial electrolytic hydrogen. Salts used in catalyst preparation were of the usual C. P. grade.

The apparatus, in its final form, consisted of a mixing tank for the reacting gases, a catalyst chamber heated by an encircling electric furnace unit, appropriate absorption trains to detect various compounds beside methane that might be formed, a partial combustion apparatus to remove hydrogen, and a final combustion apparatus.

The carbon dioxide absorption train consisted of six test-tubes, each containing 40 percent potassium hydroxide to completely remove this gas from the mixture which came from the catalyst chamber. The train (L) consisted of a tube of saturated bromine water, followed by a KOH tube. This latter should absorb any bromine carried over. The

purpose of this train was to remove any unsaturated compounds formed. The train (II) consisted of iodine pentoxide to remove any carbon monoxide by oxidation with the liberation of iodine. The various sulfuric acid tubes were in all cases to remove moisture or to keep out moisture.

The partial combustion apparatus, to remove hydrogen by oxidation, consisted of a copper oxide spiral, prepared by passing oxygen over the heated spiral, in a tube heated by an electric furnace.

The final combustion apparatus worked upon the same principle, the copper oxide in this case being heated to a much higher temperature.

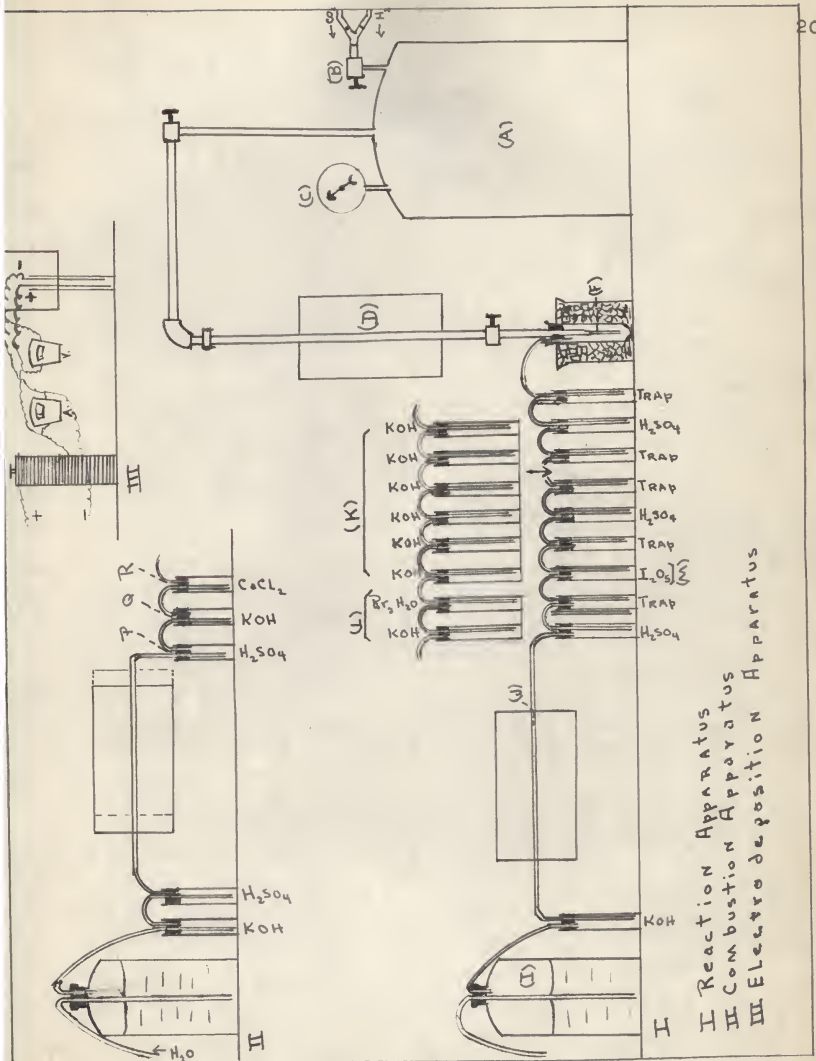
METHODS

As to the manipulation, gases were admitted under pressure from the cylinders into the mixing tank (A) thru (B), their relative concentrations being considered proportional to the difference in readings in pressure on gauge (C) as the particular gas was admitted. The gas mixtures ranged about one-fourth carbon dioxide and three-fourths hydrogen; the total pressure being between 60 and 70 pounds per square inch. Valve was then closed. After furnace (D) had been heated to an approximately constant temperature, the pyrex catalyst tube, containing the spiral catalyst, was inserted

at the opened union (E), the union closed, and the catalyst allowed to attain furnace temperature. Condenser tube (F) was then inserted into a mixture of ice and salt, the absorption train connected, the gas mixture allowed to flow into the catalyst tube, and the valve at (F) opened slightly so as to allow a flow of gas such that the rate of bubbling through the sulfuric acid tube (G) was about 20 per minute. For each run this was allowed to continue for two hours. Valve(H) was then closed and the pressure in the catalyst tube allowed to decrease gradually until slightly above atmospheric, at which point the absorption train was disconnected and the gas receiver bottle (I) stoppered and set aside for later analysis. The units of the absorption train were weighed separately to determine any gain in weight. During the run the copper oxide in tube (J) was kept at 250 degrees Centigrade at which temperature hydrogen is claimed(32) to be completely oxidized and methane completely unattacked.

The gas collected in the bottle(I) was subsequently oxidized, any hydrocarbons present being converted into carbon dioxide and water. The increase in weight of the

(32) See (1) page 441.



sulfuric acid tube (P) and of the KO tube (Q) (and the calcium chloride tube (R)) determined respectively the weight of water and carbon dioxide formed. By their ratio, one can calculate the ratio of carbon to hydrogen, and therefore, the composition of the particular hydrocarbon, unless the gas contains a mixture of them, when this value will only represent an average.

Catalyst Preparation

The nickel and cobalt catalysts were prepared by dissolving the bivalent chlorides in concentrated C. P. ammonium hydroxide and suspending in this solution a clean copper spiral, the anode being in all cases a platinum wire sealed through a glass tube with mercury for contact. Electroplating was carried out about four hours per catalyst with an amperage of about .8 and voltage between 3 and 4.

The reason for using the above method was that the usual methods of precipitation quite usually involve some adsorption of ions by colloidal particles, and long heating is necessary in attempting to volatilize impurities. High temperatures seem to decrease catalytic activity. It was hoped, therefore, that by electroplating out pure metals,

the metal would be secured in a fine state of division, and could be activated(oxidized and reduced) readily. The method worked and the catalytic surfaces were obtained. The activation temperatures were about 300 degrees, and time of oxidation ten minutes, and of reduction 20 minutes. The catalysts, following reduction, were cooled in hydrogen to prevent oxidation.

The gas mixtures collected in bottle (I) were analyzed as noted under apparatus. The method of determination of composition was by the combustion with copper oxide. The increase in weight of the KOH train was taken as approximate to the amount of carbon dioxide passed thru per run; percent of methane was calculated from the increase in weight of the KOH tube (2) and the increase in the weight of the KOH train.

RESULTS

Catalyst	Percent Conversion	Unsaturated (increase in weight of Br tube)
Co(320 degrees)	2.2	0.0 g.
Co(450 degrees)	.86	.30
Ni(320, run#2)	.57	.1
Ni(" , " #3)	.35	.1
Ni(" , " #4)	.17	.11
Ni(450)	1.65	.35

CONCLUSION

Due to the detection of a sulfide on one of the catalysts, it was discovered that the rubber gasket (T), had apparently become heated to such an extent as to react with hydrogen and form hydrogen sulfide, which is a violent poison for metallic catalysts of the type studied. This probably almost completely poisoned the various catalysts. The results therefore probably represent a very small part of the activity of these catalysts. It appears that cobalt is more active than nickel, and therefore the more easily poisoned. The persistent gain in weight of the bromine tubes indicates unsaturated compounds. It is worthy of note that the activity of the nickel catalyst was reduced when oxidized and reduced a second and a third time.

SUMMARY

Catalysts of the active metal type have been prepared in a new way--that of electrodeposition--and the studies indicate activity. Hydrocarbons, believed to be methane, were formed by the reaction of carbon dioxide and hydrogen, and there is indication of the formation of unsaturated compounds.

Date Due

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