1936

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Recommended Citation

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CATALYTIC HYDROGENATION OF FURFURAL IN THE LIQUID PHASE AT VARIOUS TEMPERATURES AND PRESSURES

by

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A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject - Inorganic Chemistry

Approved:

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Iowa State College
1936

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ACKNOWLEDGMENT

The writer wishes to express his appreciation to Dr. F. E. Brown for the suggestion of this problem, and for his advice and encouragement while carrying out the investigation.

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INTRODUCTION

Hydrogenation of both elements and compounds, practiced on the colossal scale that it is today, has evolved from the admirable investigations of Sabatier and his associates, whose studies, on the catalytic activity of finely divided nickel, copper, and other base metals were first reported in 1897, and for which, with later investigations, he was awarded the Nobel prize, in chemistry in 1912. This principle was used at about one atmosphere of pressure in the vapor phase, and since has been extended to both the vapor and liquid phase at thousands of pounds of pressure and applied to many classes of organic compounds by numerous chemists. Although a few minor reactions between molecular hydrogen and an element, or unsaturated compound, had previously been reported, Kuhlmann (25) in 1838, produced ammonia using oxides of nitrogen and hydrogen in the presence of platinum sponge; Corenwinder (15) in 1852 reported rapid reaction between hydrogen and iodine at 300°-400° in the presence of platinum; Debus (17) in 1863 hydrogenated hydrocyanic acid to produce methyl amine in the presence of platinum black; von Wilde (39) in 1874 produced ethylene and ethane by hydrogenating acetylene with a platinum black catalyst. Sabatier's work brought about the realization of the possibilities in hydrogenation to many chemists, and thereby catalyzed catalytic hydrogenation processes.

When one considers the amount of useful or more useful chemicals produced by this process from cheap or waste materials, such as the vegetable and animal oils converted to oils that can be used in the food and soap industries; the increased amount of gasoline produced from petroleum, by cracking and subsequent hydrogenation; the hydrogenation of coal; and the production of alcohols from carbon monoxide; besides the hydrogenation of nitrogen in the synthesis of ammonia, the importance of hydrogenation as a technical process can be realized.

Many compounds which are difficult or impossible to obtain directly, or are more time consuming and expensive to prepare by other methods, can readily be produced by hydrogenation. Hexahydrobenzene, for example, can be prepared easily from benzene and hydrogen in the presence of nickel, but is obtained with difficulty by other methods. Furthermore, in the proof of structure of some compounds, and in the identification of them, hydrogenation can be very useful.

Furfural, one of the products of agricultural wastes, has developed a number of important uses, such as in the resin and solvent industries; likewise the hydrogenated products of furfural are of increasing usefulness as developments take place with the study of these products and their manufacture.

This study was started with the idea of finding the temperature and pressure which would be most favorable for the hydrogenation of furfural; and to determine the relative activity of some copper and related catalysts prepared by different methods. The free energy of furfural and some of its derivatives has previously been determined in this laboratory (27).

HISTORICAL

Hydrogenation of furfural was first reported by Padoa and Ponti (29) in 1907 with the use of the vapor phase method of Sabatier and Senderen.

A summarized review of vapor phase hydrogenations of furfural is found in Table I. The liquid phase process has certain advantages over the gas phase. The by-products are fewer especially when the proper conditions are used, and this makes separations unnecessary or much easier. The speed of reaction can be increased, with advantage, to the point of saturation of the catalyst with hydrogen by the use of higher pressures of hydrogen. Cheap catalysts, such as copper, can be employed, although they are not as active at as low a temperature, nor do they drive the reaction as far as the platinum group catalysts or even nickel. The catalysts such as copper are not as easily poisoned and sometimes it is desirable to stop at an intermediate product, especially when investigating the path of a reaction.

Liquid phase hydrogenation of furfural was first reported by Wienhaus (42) in 1921. He used one atmosphere of pressure in the presence of palladium on charcoal. Investigators (1)(10)(23)(34) were soon developing cheaper

TABLE I

Summary of investigations on the vapor phase hydrogenations of furfural

Compound	Catalyst	Temp. °C.	Press. Atm.	Products	Investigators	Year
Furfural	Ni	190	1	Furfuryl alcohol	Padoa and Ponti (29)	1907
Furfural	Ni	270	1	Sylvan, pentanol-2 tetrahydrosylvan methyl propyl ketone CO and furan	Padoa and Ponti (29)	1907
Furfural	Fe	200	1	Same products as Padoa and Ponti, but, only the lower boiling materials were identified. Furan sylvan, dihydrofuran.	Pringsheim and Noth (33)	1920
Furfural	Ni	130-150	1	Furfuryl alcohol butanol-1, 4-5%	Kotake and Fujita (24)	1930
Furfural	Cu, Ni	175-275	1	Furfuryl alcohol 5%	Brown, Gilman, Van Peursem (8)	1932
Furfuryl Alcohol	Ni	190	1	Sylvan, pentanol-2 tetrahydrosylvan methyl propyl ketone	Padoa and Ponti (29)	1907
Furan	Ni	170	1	Tetrahydrofuran, butanol-1	Bourguignon (5)	1908
Sylvan	Os	80-82	1	Tetrahydrosylvan	Zelinski and Schuikin (44)	1934
Sylvan	Pt	<100	1	no change	Zelinskin and Schuikin (44)	1934
Sylvan	Pt	160	1	Tetrahydrofuran tetrahydrosylvan butanol-2, pentanol-2	Zelinskinand Schuikin (44)	1934

catalysts than palladium and platinum, although to be practical these cheaper catalysts required the use of high temperatures and pressures to secure rapid rates of reaction.

A summary of previous work on liquid phase hydrogenations is found in Table II. It is apparent from these investigations that Cu-Cr oxide or modifications of it are better than Ni catalysts for the production of furfuryl alcohol. Also, that practically the only product obtained when using temperatures of 200° or less is furfuryl alcohol (1)(10)(34), especially if the product is cooled and removed from the hot vessel as soon as the necessary equivalents of hydrogen are absorbed.

It is known that primary alcohols undergo hydrogenolysis (defined by Connor and Adkins (12) as, "The cleavage of C to C or C to O bonds accompanied by the addition of hydrogen.") to produce hydrocarbons of one less carbon atom (43). Also furfuryl alcohol is known to hydrogenolyze in the presence of Cu-Cr oxide (1)(12) and Ni (23) and furthermore, it has been observed that sylvan, furfural and water are produced from furfuryl alcohol in contact with metal oxides at temperatures around 400°C. without the presence of hydrogen by autoxidation (31).

An examination of earlier work also shows that Ni is a better catalyst than Cu-Cr oxide for the hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol. Komotsu and

TABLE II

Summary of investigations on liquid phase hydrogenation of furfural and some related compounds

Compound	Catalyst	Temp. °C.	Press. Atmos.	Products	Invest-igators	Year
Furfural	Pd on C	Room	1	Tetrahydrofurfuryl alcohol	(42)	1921
Furfural in ethyl alcohol	Pt and $FeCl_2$	50 -60 1 hr.	1-2	Furfuryl alcohol	(20)	1923
Furfural	Ni	160 6 hrs.	100	Furfuryl alcohol, furan and methylfuran	(23)	1930
Furfural	Cu - Cr	150 2 hrs.	100-150	Furfuryl alcohol	(1)	1931
Furfural	Cu-Cr and $Ca(OH)_2$	175 .5 hrs.	50-100	Furfuryl alcohol	(10)	1934
Furfural	Cu-Cr and CaO	200	100	Furfuryl alcohol	(34)	1935
Furfural diacetate	Pd on C	Room 6 hrs.	1	Tetrahydrofurfurol after hydrolysis	(36)	1924
Furfural diacetate	Ni	160 3.5 hr.	100-200	2-methyltetrahydrofuran 10%, acetic acid 78%, tetrahydrofurfuryl acetate 41%, tetrahydrofurfural diacetate 24%.	(9)	1934
Ethyl acetal of furfural	Ni	175 5 hrs.	200	Tetrahydrofurfural upon hydrolysis	(16)(28)	1933
Furfuryl alcohol	Pd on C	Room	1	Tetrahydrofurfuryl alcohol	(42)	1921

TABLE II (Cont'd.)

Compound	Catalyst	Temp. °C.	Press. Atmos.	Products	Invest-igators	Year
Furfuryl alcohol in ethyl alcohol	Pt and $FeCl_2$	50-60 4 hrs.	1-2	Tetrahydrofurfuryl alcohol n-amyl alcohol pentanediol-1, 2 pentanediol-1, 5	(20)	1923
Furfuryl alcohol	Ni	144 ? hrs.	80	Dihydrofurfuryl alcohol	(23)	1930
Furfuryl alcohol	Ni	180 7 hrs.	85	Tetrahydrofurfuryl alcohol 70%	(23)	1930
Furfuryl alcohol	Ni	300 13 hrs	90	Tetrahydrofurfuryl alcohol, tetrahydrofuran, tetrahydrosylvan	(23)	1930
Furfuryl alcohol	Cu-Cr	175 11.5 hr.	100-150	Amyl alcohol 10%, methyltetrahydrofuran some, tetrahydrofurfuryl alcohol some, pentanediol-1, 2) pentanediol-1, 5) 70%	(1)	1931
Furfuryl alcohol	Cu-Cr	250 4 hrs.	175	Methylfuran 36%, n-pentane 0.3%, pentanol-1 36%, furfuryl and tetrahydrofurfuryl alcohol 13%, 125%? pentanediol-1,2 14%, pentanediol-1,5 15%, intermediates and residue 11%	(12)	1932
Furfuryl alcohol	Cu-Cr	250 57.5 hrs	175	Methylfuran 20%, pentanol-1 10%, furfuryl and tetrahydrofurfuryl alcohol 17%, 86% pentanediol-1,2 14% pentanediol-1,5 15% intermediate and residue 10%	(12)	1932
Furfuryl alcohol	Ni	125 2.5 hrs	100-200	Tetrahydrofurfuryl alcohol 85%	(9)	1934

TABLE II (Cont'd.)

Compound	Catalyst	Temp. °C.	Press. Atmos.	Products	Investigators	Year
Tetrahydrofurfuryl alcohol in ethanol	Pt and $FeCl_2$	50-60	1-2	No hydrogenation	(20)	1923
Tetrahydrofurfuryl alcohol	Ni	300 8 hrs.	30	Tetrahydrofuran methyltetrahydrofuran n-butyl alcohol tetrahydrofurfuryl ether	(23)	1930
Tetrahydrofurfuryl alcohol	Cu-Cr	250 11 hrs	175	Methyltetrahydrofuran and H_2O 5%, tetrahydrofurfuryl alcohol 77%, pentanediol-1,5 13%	(12)	1932
Pentanediol-1,2	Cu-Cr	250 10 hrs	175	Pentanediol-1,2 73% amyl alcohols, traces of butanol, methanol 26%	(12)	1932
Methylfuran	Cu-Cr	250 4 hrs.	175	n-pentane 4%, methyltetrahydrofuran 15%, pentanol-2 33%, pentanol-1 30%, intermediates, residue and loss by drying 15%	(12)	1932
Methylfuran	Ni	250 2 hrs.	175	Methyltetrahydrofuran 83%, methylfuran 6%	(12)	1932
Methyltetrahydrofuran	Cu-Cr	250 6 hrs.	175	Methyltetrahydrofuran 74%	(12)	1932
Furan	Pd-PdO	Room 20 hrs	7	Tetrahydrofuran 95%	(38)	1934

Masumoto (23) obtained a 70% yield of tetrahydrofurfuryl alcohol at 180° and 85 atmospheres during 7 hours over Ni, and Burdick and Adkins (9) report an 85% yield of tetrahydrofurfuryl alcohol in 2.5 hours using a Ni catalyst at 125° and 100-200 atmospheres of pressure. In contrast to this Adkins and Connor (1) obtained a 70% yield of pentanediols-1, 2 and 1, 5 by using Cu-Cr oxide catalyst at 175° and 100-150 atmospheres of pressure for 11.5 hours.

In the preparation of pentanediols 1, 2 and 1, 5 from furfuryl alcohol, Cu-Cr oxide is better than a Ni catalyst. This is shown by Adkins and Connor's (1) report of a 70% yield over Cu-Cr oxide catalyst at 175° and 100-150 atmospheres of pressure for 11.5 hours, as opposed to the fact that Komatsu and Masumota (23) found no pentanediols when treating furfuryl alcohol with hydrogen over nickel at 300° and 90 atmospheres for 13 hours.

It is also of interest to note that Connor and Adkins (12) found that tetrahydrofurfuryl alcohol gives pentanediol-1, 5 upon hydrogenolysis and not a mixture of glycols as is produced from furfuryl alcohol.

It is further noted that Komatsu and Masumoto (23) are the only investigators to report the formation of dihydrofurfuryl alcohol from furfuryl alcohol. Although their only means of identifying the compound was by physical constants, they did get hydrogenation curves to support their views.

In addition to the work summarized in Table II, Burdick and Adkins (9) did some very interesting work on the hydrogenation of B-furylacrolein, a molecule which has a number of possibilities, i. e., ring or side chain saturation, hydrogenation of the aldehyde group or hydrogenolysis of the ring or the side chain. Nickel and Cu-Cr oxide catalysts were used with the following results:

Catalyst	Temp.	Press.	Main Products
Ni on kieselguhr	160°	100-200 atmos.	1,5-dioxaoctahydroindene 33%
Raney Ni in ethanol	160°	" "	3 tetrahydrofurylpropanol 65%
Raney Ni in ethanol	23°	" "	B furylpropionaldehyde 64%
Cu-Cr oxide in ethanol	120-175°	" "	3-furylpropanol 72%
Cu-Cr oxide in ethanol	200°	" "	heptanediol-1,4 29% heptanediol-1,7 20% n-heptanol 4% 3-tetrahydrofurylpropanol 22%

These products were expected by the authors, with the exception of the first one indicated in the table. The Cu-Cr oxide catalysts tend to split the furan ring, whereas the nickel catalysts tend to saturate the furan nucleus. Among the previous investigations Roberti (34) reports the only study to determine the optimum conditions for the hydrogenation of furfural to furfuryl alcohol. He, however, determined only the temperature effects at 200° and less, when using a pressure of 100 atmospheres, and compared the activity of the catalysts, Cu, Cu-Ni, Ni, and Cu-Cr oxide, including a catalyst (37 K.A.F.) prepared according to directions of Adkins, Connor and Folkers (14).

No reports have been made on the determination of the lowest pressure that would produce a rate of reaction which would not be increased to any large extent by higher pressures.

Roberti (34) found the Cu-Cr oxide catalyst gave almost quantitative yields of furfuryl alcohol when using 200° and 100 atmospheres of pressure. He also noted that the addition of alkaline earth oxides, especially calcium oxide, lengthens the life of the catalyst.

Calingaert and Edgar (10) found that by adding 20 grams of slaked lime per liter of furfural the product was lighter in color and the rate of hydrogenation was increased.

Connor, Folkers, and Adkins (14) report that, by adding certain barium, calcium or magnesium salts in the preparation of their catalysts, more rapid hydrogenations took place because the calcium,barium, or magnesium kept the catalyst from being reduced. Of the various Cu-Cr oxide catalysts used by them, the most active one contained calcium.

In this connection, the above authors also found that a Cu-Cr oxide catalyst which contained no barium (20 R.A.C.) failed to hydrogenate ethyl caprylate appreciably, and was bright red in color after the attempted reaction, whereas a Cu-Cr oxide catalyst which contained barium (22 R.A.C.) produced 90% hydrogenation of the ester after 7.25 hours, and was black in color when it was removed from the reaction mixture. Furthermore, the above two catalysts were very similar in their activity for the hydrogenation of furfural or acetone, and this caused them to believe that the barium stabilized the catalyst against reduction.

This latter view is in opposition to that held by Schmidt (37) who believes the hydrogenating properties of catalysts are connected with the metallic state and that oxides of metals are effective only at temperatures at which they are at least partially reduced by hydrogen to metals. Two types of hydrogenating catalysts are noted, (1) mono- and bivalent elements, including the alkalies and alkaline earths, which form solid, salt-like hydrides and whose atomic volumes are located at the maxima of the long periods, (2) bivalent elements or those which have a minimum or a maximum valence of 2 and do not form solid hydrides but do form solutions with hydrogen, and whose atomic volumes are located at the minima of the long periods. Iron and platinum groups and copper, chromium, manganese and rhenium, belong to this class.

Schmidt believes that catalytic hydrogenation is an ionic catalysis, and that the electrons in the first class, and the ions of the metal in the second class, are the real catalysts. In the second class, the valence electrons are free and mobile in the interior of a metal leaving ions rather than atoms. These ions carry strong electric fields in their vicinity and in these strong fields hydrogen is ionized to form positively charged ions.

EXPERIMENTAL

Apparatus

The hydrogenations were made in a rocking type, cylindrical, copper lined, steel autoclave approximately 3 feet in length, with an inside diameter of about 3 inches, and having a capacity of nearly 3.85 liters. One end of the cylinder was open and could be closed by the use of a steel head, with either a copper or lead gasket and eight stud bolts of one-half inch diameter. A valve and a threaded connection in the center of the head provided an inlet and outlet for the hydrogen. The power to rock the autoclave was supplied by an electric motor, which produced 27 cycles of the vessel per minute.

The reaction vessel was heated by means of an electrical resistance unit, made of nichrome wire molded in alundum cement, properly insulated with asbestos on the outside and then covered with an outer galvanized iron jacket.

The pressure changes were followed by a gauge mounted on the top of the autoclave in the center of its long axis. The temperature was determined by the use of a calibrated thermometer in a thermometer well, located in a steel collar near the supports, or axis, on which the vessel rocked.

This method of obtaining the temperature necessitated a calibration to determine the temperature of the liquid inside the autoclave from the thermometer readings in the well.

Calibration to determine the temperature of the liquid, inside the autoclave from the thermometer readings in the well.

Two hundred fifty ml. of glycerine were placed in the autoclave. This was the volume of furfural that was used in the hydrogenations. A wooden plate, gasketed by lead, was used to close the autoclave. This plate had two holes through which the insulated wires of the iron-constantan (No. 20 Leeds and Northrup) thermocouple extended. These holes were made liquid tight by driving small wooden plugs into the openings from the inner side.

The thermocouple was placed on the inside, near the center of the autoclave, and the wires were insulated from each other and from the sides of the vessel by means of glass tubes so arranged that the liquid could flow freely in contact with the thermocouple when the bomb was in motion.

A thermometer was also placed in contact with the liquid through another hole in the wooden plate made liquid tight by using an ordinary cork. This was used as a further check on the temperatures inside of the vessel.

A second calibrated thermometer was placed in the thermometer well and the E.M.F. readings, and readings on the two thermometers, were taken simultaneously every five minutes, except near the maximum temperatures used, when they were taken every two and a half minutes.

The heating unit was connected directly to the 220 volt line and allowed to heat the bomb and its contents as rapidly as it would, until the thermometer reading in the well was 160°. Then the heating unit was disconnected and the bomb and its contents were allowed to cool. Readings were made until the thermometer in the well recorded 130°C. This same heating method was used in the hydrogenations.

The E.M.F. was measured with a Leeds and Northrup portable potentiometer, using a cold junction of 0°C. in place of the compensator and the compensator was set on 0°. The iron-constantan couple was connected on the noble metal range, which enabled the readings to be made to 0.02 millivolt or 0.4 of a degree. The millivolt readings were converted to the correct temperatures by means of a Leeds and Northrup conversion table.

A graph was then constructed using the thermometer readings in the well as the abscissa, and the amount of correction to be added in each case as the ordinate. This curve was then used to obtain the correct temperature of the liquid at any time from the readings of the thermometer in the well.

Calibration of the autoclave to determine the moles of hydrogen used per 100 pound drop in pressure.

The volume of hydrogen obtained for a 50 pound drop in gauge reading, from 900 to 850 pounds, was measured over water at 20°C. and 747 mm. and then from this was calculated the volume of hydrogen at 0°C. and 760 mm. It was thus determined that a 50 pound drop in pressure was equivalent to 0.4979 moles of hydrogen. This result was checked by a drop in pressure from 1400 to 1350 pounds.

Preparation of Catalysts

Cu-Cr oxide, Catalyst No. 1

This catalyst was prepared according to the directions of Connor, Folkers, and Adkins (13).

Seventy-one grams of $(NH_4)_2CO_3 \cdot H_2O$ in 400 ml. of water were added to a solution containing 50 grams of $Cu(NO_3)_2 \cdot 3H_2O$, 5.4 grams of $Ba(NO_3)_2$ and 77 grams of $Cr_2(NO_3)_6 \cdot 15H_2O$ in 575 ml. of water. The mixture was stirred well, filtered on a Büchner funnel and washed twice with 50 ml. portions of H_2O. It was then dried over night at 110°C., powdered and decomposed by heating to 230°C.

Cu-Cr oxide, Catalyst No. 2

The same directions were used as in Number 1, except that the heating was limited to 130-150°C., after drying over night and powdering, instead of heating to 230°C.

Cu_2O, Catalyst No. 3

Five hundred ml. of water were saturated with $CuSO_4 \cdot 5H_2O$ and NaCl and the copper subsequently reduced by bubbling SO_2 gas into the solution until the change appeared to be complete. The excess SO_2 was then driven out by boiling the solution for 20-30 minutes.

A saturated solution of sodium carbonate was added to the well stirred hot solution until effervescence ceased; the precipitated Cu_2O was washed three times by decantation, filtered and washed several times, then dried over night in a vacuum desiccator, and powdered. It was then ready for use.

Cu_2O, Catalyst No. 4

Five hundred ml. of a 40% sodium hydroxide solution were added gradually with stirring to a solution containing 500 grams of dextrose and 500 grams of $CuSO_4 \cdot 5H_2O$ in 2500 ml. of water. The mixture was then warmed on a water bath to about 85° for 30 minutes, filtered with a Büchner funnel, washed until the filtrate was clear, dried over night in a vacuum desiccator, powdered and stored in a stoppered bottle until used. One hundred forty grams of catalyst was obtained. Mellor (26) states this Cu_2O is stable in air and free from hydroxide.

Sarma (35) claims the compound is very stable and can be heated to 150° after drying without changing color. It contains 82% Cu when dried at 110° and he believes $Cu(OH)_2$ is present in the precipitate.

Cu_2H_2, Catalyst No. 5 (Method of Vörlander and Meyer (40)

One hundred grams of $CuSO_4 \cdot 5H_2O$ were dissolved in 400 ml. of water and warmed to 60-70°C. on a water bath. Then 106 grams of 50% hypophosphorous acid, which had previously been warmed to 60°C., were added. After 10-15 minutes, the mixture was filtered and the precipitate was washed several times, dried in a vacuum desiccator for four hours, and used immediately. If the compound was dried for more than four hours it oxidized upon exposure to air.

Cu-Ur oxide, Catalyst No. 9

Seventy one grams of $(NH_4)_2CO_3 \cdot H_2O$ in 400 ml. of water were added to a solution made of 50 grams of $Cu(NO_3)_2 \cdot 3H_2O$ and 5.4 grams of $Ba(NO_3)_2$ and 50 grams of $UO_2(NO_3)_2 \cdot 6H_2O$ in 575 ml. of water. After stirring the mixture was filtered on a Büchner funnel, dried on a hot plate and heated to 160°C., powdered, and stored in a stoppered bottle until used.

Cu-Cr oxide, Catalyst No. 12

A concentrated solution of CrO_3 in water was made and powdered $CuCO_3$ added until effervesence ceased. Then concentrated ammonium hydroxide was added to this mixture until precipitation seemed to be complete. The mixture was allowed to dry in the air, pulverized, dried in a vacuum desiccator, heated to 160°C. and stored in a stoppered bottle until used.

Cu-Cr oxide, Catalyst No. 13

This catalyst was prepared according to directions of Calingaert and Edgar (10).

One half mole (149 grams) of $Na_2Cr_2O_7.2H_2O$ and 1 mole (250 grams) of $CuSO_4.5H_2O$ were dissolved in 1200 ml. of water. To this solution was added slowly 2 moles of concentrated NH_4OH (the exact end point is reached when a few drops of a filtered sample gives no further precipitation when NH_4OH is added) filtered, and washed until the wash water was colorless. The solid was dried at 110° and then heated to 320°-340°C.

Cu-Cr oxide, Catalyst No. 23

This catalyst was prepared according to the directions of Connor, Folkers and Adkins (14).

Five and four-tenths grams of $Ba(NO_3)_2$ were dissolved in 50 ml. of boiling water. Seventy-seven and two-tenths grams of $Cr_2(NO_3)_6 \cdot 15H_2O$ were dissolved in 450 ml. of warm water, and 100 grams of $Cu(NO_3)_2 \cdot 3H_2O$ were dissolved in 150 ml. of water. The three solutions were mixed at 35°C. and 94.4 grams of $(NH_4)_2CO_3 \cdot H_2O$ in 535 ml. of water were added. The mixture was filtered on a Büchner funnel, washed with two 50 ml. portions of water, dried at 110-120°, pulverized, and decomposed in two portions by heating to 190-230°.

The powdered product was then suspended in 100 ml. of a 10% acetic acid solution, filtered, washed with two 75 ml. portions of water and dried at 110-120°.

Cu_2O, $Ca(OH)_2$ Catalyst No. 26

One hundred fifty ml. of a 40% sodium hydroxide solution were added, with stirring to a solution composed of 43.8 grams of $Ca(NO_3)_2$, 100 grams of $Cu(NO_3)_2 \cdot 3H_2O$ and 100 grams of dextrose in 400 ml. of water. The mixture was warmed on the water bath at 85° for 30 minutes, filtered on a Büchner funnel through a number 42 Whatman filter paper, washed until the filtrate was clear, dried for 12 hours in a vacuum desiccator, powdered and stored in a stoppered bottle until used.

Method of Procedure

Two hundred fifty ml. (approximately 3 moles) of furfural were placed in the autoclave, and 8.6 grams of catalyst added, except where otherwise indicated. Then the vessel was closed and 500 pounds of hydrogen added and subsequently vented off to remove the air. The desired pressure of hydrogen was then added and the apparatus allowed to stand for two or more hours to detect any leaks present. If no drop in pressure took place during this time the autoclave was started in motion.

The time, temperature, and pressure were recorded and the heating units were connected directly to the 220 volt line, and the autoclave allowed to heat up as rapidly as it would, until the reading of the thermometer in the well reached 160°. Then the heating units were disconnected.

The rocking motion of the bomb was continued, until the reading of the thermometer in the well was about 130°. Temperature, and pressure readings were taken every five minutes during this heating and cooling period. This rate of heating and cooling was the same as the rate under which the liquid temperatures were determined when calibrating the autoclave.

The vessel and contents were allowed to cool overnight and the pressure and temperature readings taken again.

The two readings at room temperatures were used to calculate the total amount of hydrogen used in each hydrogenation.

The hydrogen was vented off and the products were drained out. Between experiments the autoclave was thoroughly cleaned by the use of a scraper and cloth swabs.

Method of determining the rate of hydrogenation and the total amount of hydrogen used

The observed pressures were first converted to absolute pressures by adding 14.7 pounds, and these pressures at the observed temperatures were calculated to the theoretical pressures at 0°C. using the simple gas laws. These pressures at 0°C. were used to find the drop in pounds of pressure at 0°C. for the five minute intervals. Graphs were then constructed with pounds of hydrogen used at 0°C. as the ordinate and time in minutes as the abscissa.

It was noted that the calculated pressure at 0°C. increased slightly from the start to a certain point and then decreased again. This increase was no doubt due to the vapor pressure of the furfural and decreased solubility of the hydrogen as the temperature increased up to the beginning of the hydrogenations. Therefore the highest calculated pressure at 0°C. was taken as the point of the start of hydrogenation.

To calculate the total amount of hydrogen used, the above calculations were made by using the temperature and pressure readings before starting, and after the completion of the experiment, when the autoclave was at room temperatures.

Method of finding the amount of furfuraldehyde in the product

In addition to following the drop in pressures with time, it seemed advisable to check the aldehyde content of the product and calculate it as furfural.

The total aldehydes were titrated with the use of an excess of potassium hydrogen sulfite. This method was reported to be accurate (30)(19), especially when using an excess of bisulfite. Other investigators (22) claim it is only about 98% correct when working with 0.1 N solutions and with bisulfite in at least a three fold excess over the theoretical amount necessary. In controls run in this laboratory when working at about 5°C., results were correct to within nearly 3%. The dissociation constant falls sharply with temperature (21).

After allowing the suspended catalyst to settle from the product for 24 hours, nearly 4 grams of the liquid were weighed accurately, and made up to 1 liter at 20°C., in a volumetric flask. Three samples of 10 ml. each were pipetted into separate 50 ml. Erlenmeyer flasks. Ten ml. of potassium bisulfite solution (12 grams per liter) were added to each flask from a burette. The mixture was allowed to reach equilibrium in a refrigerator at about 5°C. for 24 hours and titrated quickly with a 0.1 N iodine solution using starch as an indicator. Three blanks were run at the same time.

The hydrogenation products of furfural by the use of Cu-Cr oxide catalysts have been so thoroughly investigated by Adkins and his students that little work was done on the identification of the minor substances produced.

The product was generally distilled under reduced pressure with a special fractionating column. It was noted, in the cases where approximately three moles of hydrogen were used, that nearly a quantitative yield of furfuryl alcohol was obtained, as determined by the temperature at which distillation took place.

Results

Explanation of the items listed in the Tables 3, 4, 5, 6, 7, 8, and 9.

Experiment number. A keyed system is used. The first or first two numbers before the letter indicates the hundreds of pounds of pressure when the apparatus was at room temperature before the experiment was started.

The first letter indicates different experiments carried out with the same catalyst; "a" for the first, "b" for the second, etc.

The last number gives the number of the catalyst used, and, when followed by a letter, the letter indicates that some compound was used with the catalyst. The compound indicated by each letter used in this way is indicated in the table in which it is used.

Reaction starts at °C. The temperature at which reaction starts was determined from the pressures calculated to 0°C., as explained previously, these calculated pressures increased slightly as the temperature of the apparatus was raised, and the slight increase in pressure was due to the increased vapor pressure of the furfural, and the decreased solubility of hydrogen, at the higher temperatures. Therefore the highest calculated pressure at 0°C. was taken as the point where hydrogenation started, and the temperature of the liquid so recorded.

Reaction starts at pounds. The absolute pressure at the time the reaction starts.

Moles of hydrogen used. The moles of hydrogen used was calculated from the temperature and the pressure when the autoclave was at room temperatures before and after the hydrogenation, and is the total moles of hydrogen reacted.

Time to react with 2.25 moles of hydrogen. The time to react with 2.25 moles of hydrogen was chosen because it is the point where three-fourths of the furfural might have reacted to form furfuryl alcohol if no other compound formed. The time was determined from the graphs and was the number of minutes from the time that reaction started until 2.25 moles of hydrogen had reacted.

The other items are self explanatory.

Discussion of the results in Tables 3 and 4 and Figures 1, 2 and 3.

An inspection of Tables 3 and 4 shows that hydrogenation starts between the temperatures of 146-168°, and is independent of the pressure when using initial pressures of hydrogen from 200 to 1,800 pounds.

There is no noticeable difference in the amount of furfural left in the product, or the total amount of hydrogen reacting when initial pressures of 800 to 1,800 pounds are used. At initial pressures of 400 pounds, and less, the rate of reaction and the amount of hydrogen reacting are decidedly decreased.

The temperature for the greatest rate of hydrogenation is not below 208° when using the 8.6 grams of Cu-Cr oxide catalyst Number 2 in 250 ml. of furfural.

Tables 3 and 4 show that the drop in pressure of hydrogen, for the five minute interval of greatest reaction, increases only slightly with an increase of pressure.

TABLE III

Results obtained by hydrogenating furfural at different pressures, with Cu-Cr oxide catalyst number two

Experiment Number	18a2	16b2	14b2	12c2	*12b2	10a2
Pounds used at the start	1800	1600	1400	1200	1200	1000
Reaction starts at °C.	146	168	146	152	149	157
Reaction starts at pounds	2555	2315	1940	1715	1710	1440
Per-cent of furfural in the product	2.71	00	1.48	00	00	4.57
Moles of H_2 used	2.81	2.69	2.81	2.92	2.96	2.87
Temperature range at greatest pressure drop	208 to 216	216 to 225	229 to 236	219 to 227	200 to 209	221 to 229
Pounds of H_2 used during greatest pressure drop	146 to 203 or 57	105 to 164 or 59	200 to 250 or 50	146 to 194 or 48	163 to 219 or 56	184 to 233 or 49
Temperature at maximum pressure	190	199	196	194 and 203	171	189
Maximum pressure	2720	2425	2125	1815	1740	1490
Time to react with 2.25 moles of H_2	39	40	50	47	34	43

*17.2 g. of catalyst used or twice the usual amount

TABLE IV

Results obtained by hydrogenating furfural at different pressures, with Cu-Cr oxide catalyst number two

Experiment Number	8a2	6a2	4a2	2a2
Pounds used at the start	800	600	400	200
Reaction starts at °C.	146	152	164	168
Reaction starts at pounds	1115	845	590	300
Per-cent of furfural in the product	1.93	1.85	13.45	55.17
Moles of H_2 used	2.96	2.68	2.28	1.25
Temperature range at greatest pressure drop	223 to 231	213 to 221	227 to 237	218 to 225
Pounds of H_2 used during greatest pressure drop	154 to 198 or 44	91 to 128 or 37	101 to 146 or 45	27 to 40 or 13
Temperature at maximum pressure	179 and 190	173 and 186	186	192
Maximum pressure	1165	875	605	310
Time to react with 2.25 moles of H_2	51	49	did not	did not

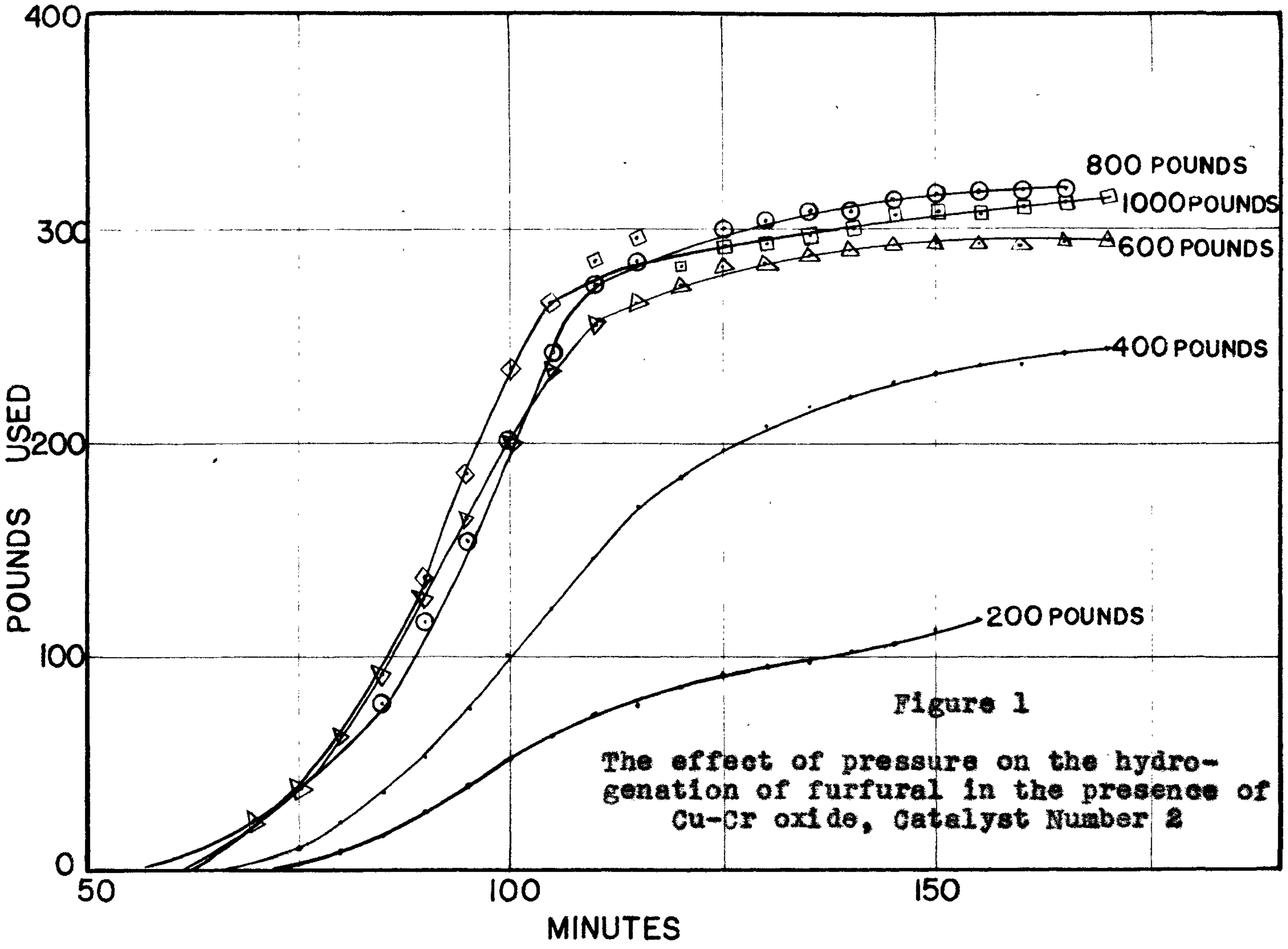


Figure 1

The effect of pressure on the hydrogenation of furfural in the presence of Cu-Cr oxide, Catalyst Number 2

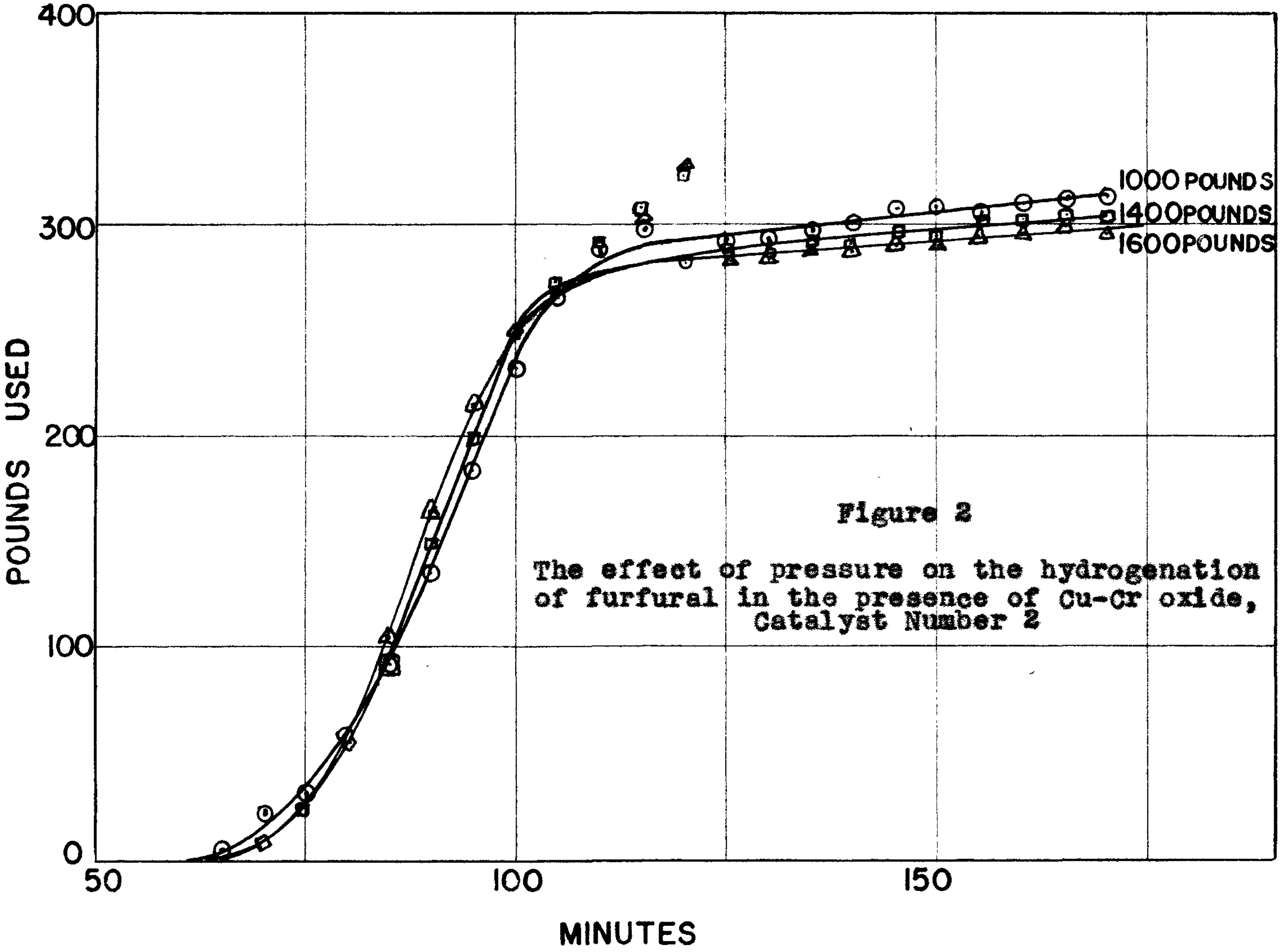


Figure 2

The effect of pressure on the hydrogenation of furfural in the presence of Cu-Cr oxide, Catalyst Number 2

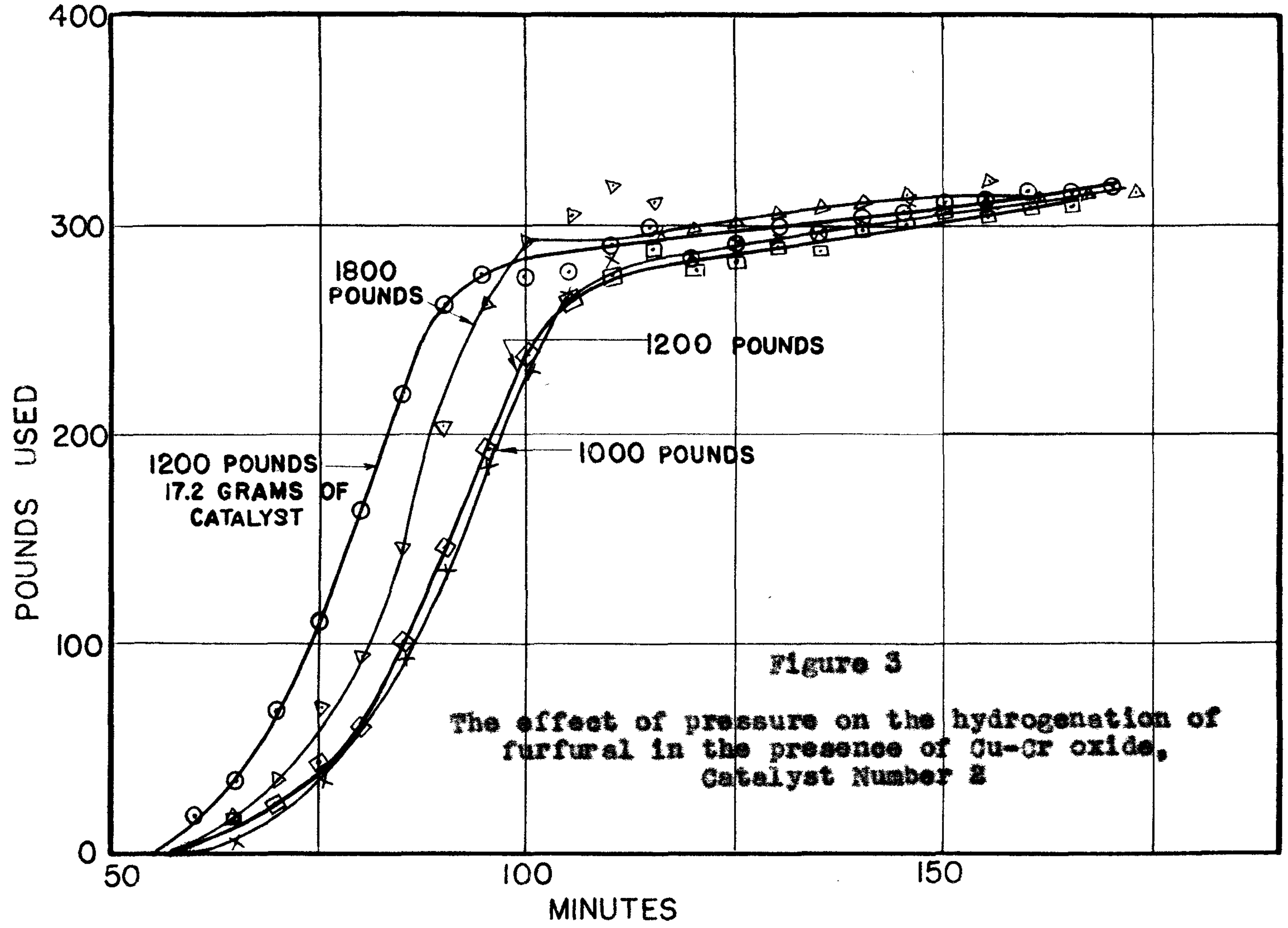


Figure 3

The effect of pressure on the hydrogenation of furfural in the presence of Cu-Cr oxide, Catalyst Number 2

It is evident from Figures 1, 2, and 3 that the only advantage to be gained by higher initial pressures than 800 pounds, is a slight increase in rate.

Table 3 and Figure 3 show that doubling the amount of catalyst produces only a slight increase in the rate, and the amount, of hydrogen reacting, at an initial pressure of 1,200 pounds.

Discussion of the results of Table 5 and Figure 4

It has been reported that calcium and barium compounds have a favorable influence on the hydrogenation of furfural with Cu-Cr oxide catalysts (14)(10). The method of preparing the catalyst by precipitating the barium or calcium from the nitrates, with the copper and chromium, and then washing the precipitate, leaves an unknown amount of these elements in the final catalyst. A better idea of the effect of each can probably be obtained by adding a known amount of the calcium oxide or barium oxide after the catalyst has been prepared.

In the hydrogenations reported in Table 5, 8.6 grams of catalyst were used, and 5 grams of the compound mentioned in the respective experiments, except in experiment Number 14a12a where 10 grams of $Ca(OH)_2$ were used.

The temperature at which reaction with hydrogen starts is raised about 24 degrees by using BaO, $Ba(OH)_2$ or $Ba(OH)_2 8H_2O$ with Cu-Cr oxide catalyst Number 12. The CaO and

TABLE V

Results on hydrogenation with Cu-Cr oxide catalyst number 12 in the presence of BaO, $Ba(OH)_2$, $Ba(OH)_2 \cdot 8H_2O$, CaO and $Ca(OH)_2$. at 1400 lbs. starting pressure

Experiment Number	14al2e	14al2a	14al2d	14al2	14al2c	14al2b
Catalyst used, CuCrl2 +	CaO	$Ca(OH)_2$	$Ba(OH)_2$		BaO	$Ba(OH)_2 \cdot 8H_2O$
Reaction starts at °C.	155	155	182	149	183	183
Reaction starts at pounds	1905	1995	2150	1980	2160	2165
Per-cent of furfural in the product	2.39	00	00	.41	00	20.76
Moles of H_2 used	3.09	2.98	2.90	2.91	2.63	2.02
Temperature range at greatest pressure drop	178 to 189	221 to 230	224 to 231	230 to 237	234 to 237	233 to 237
Pounds of H_2 used during greatest pressure drop	50 to 136 or 86	140 to 213 or 73	149 to 221 or 72	188 to 242 or 54	134 to 192 or 58	48 to 82 or 34
Temperature at maximum pressure	167	196 and 205	199	199 and 207	210	227 and 233
Maximum pressure	1930	2140	2205	2160	2235	2315
Time to react with 2.25 moles of H_2	24	43	32	51	42	did not

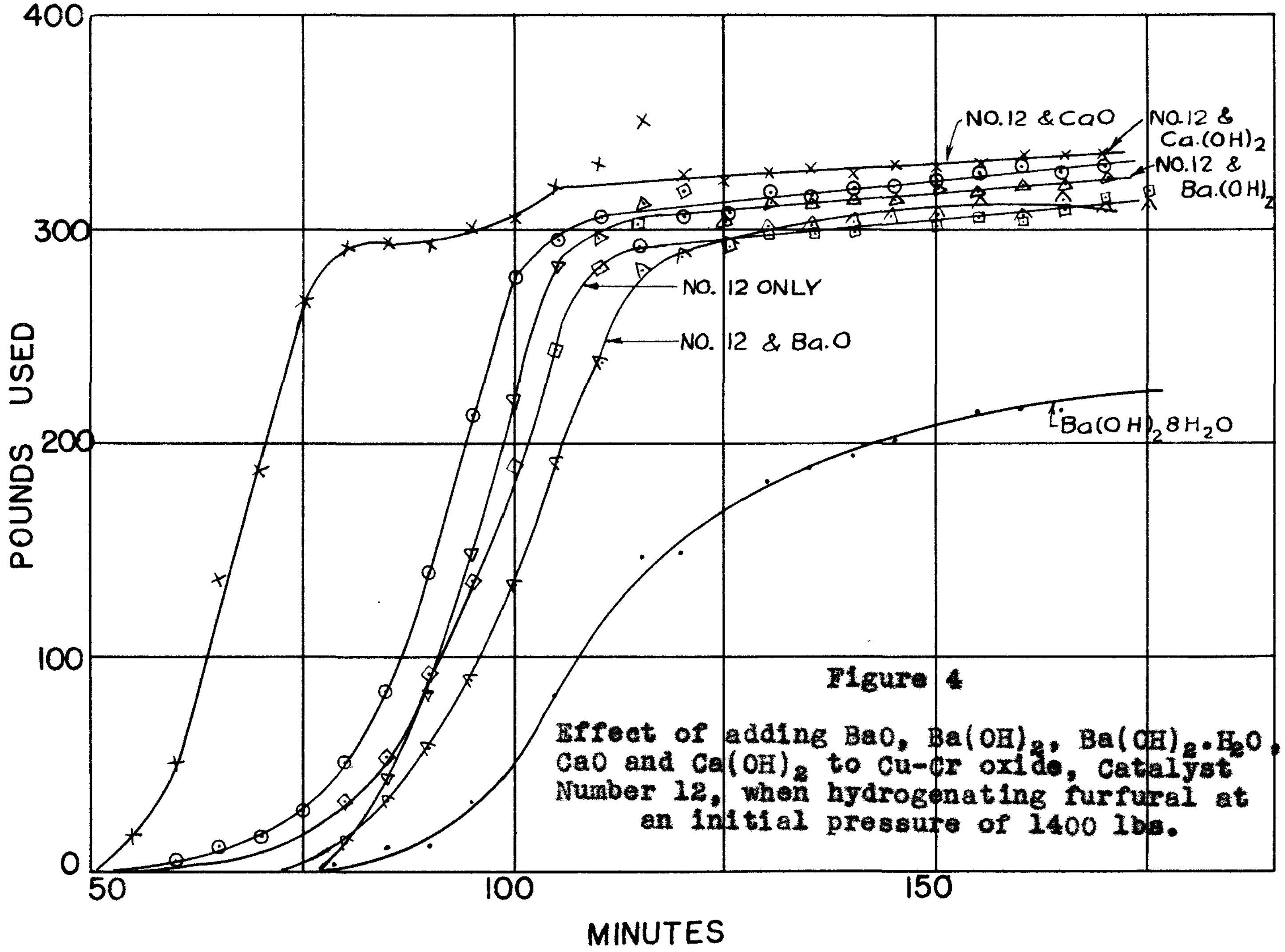


Figure 4

Effect of adding BaO, Ba(OH)$_2$, Ba(OH)$_2$·H$_2$O, CaO and Ca(OH)$_2$ to Cu-Cr oxide, Catalyst Number 12, when hydrogenating furfural at an initial pressure of 1400 lbs.

$Ca(OH)_2$ raised the starting temperature about 6 degrees.

The outstanding results in this table and figure are in the CaO and $Ba(OH)_2 8H_2O$ experiments.

A comparison of experiment Number 14a12d with 14a12b shows that water had no effect on the temperature at which hydrogenation started, but it had considerable influence on the amount of furfural left in the product, and on the total moles of hydrogen which had reacted.

The greatest rate of reaction was not below 178°C. when using 1,400 pounds of hydrogen in the presence of Cu-Cr oxide catalyst Number 12 and CaO. This is the combination that produced the greatest rate of reaction with hydrogen.

Figure 6 shows the rate of hydrogenation of furfural with Cu-Cr oxide catalyst Number 12 and 5 grams of CaO to be markedly better than other combinations.

Discussion of the results of Table 6 and of Figure 5

In the experiments reported in Table 6 and Figure 5, 8.6 grams of Cu_2O (prepared by reduction with dextrose) and 0.089 moles of the compound mentioned in the different experiments were used. The Cu_2O was prepared in a large enough quantity, so that all of the experiments in Table 6 and Figure 5 were made with Cu_2O which had been prepared at the same time, except one of the Cu_2O curves in Figure 5.

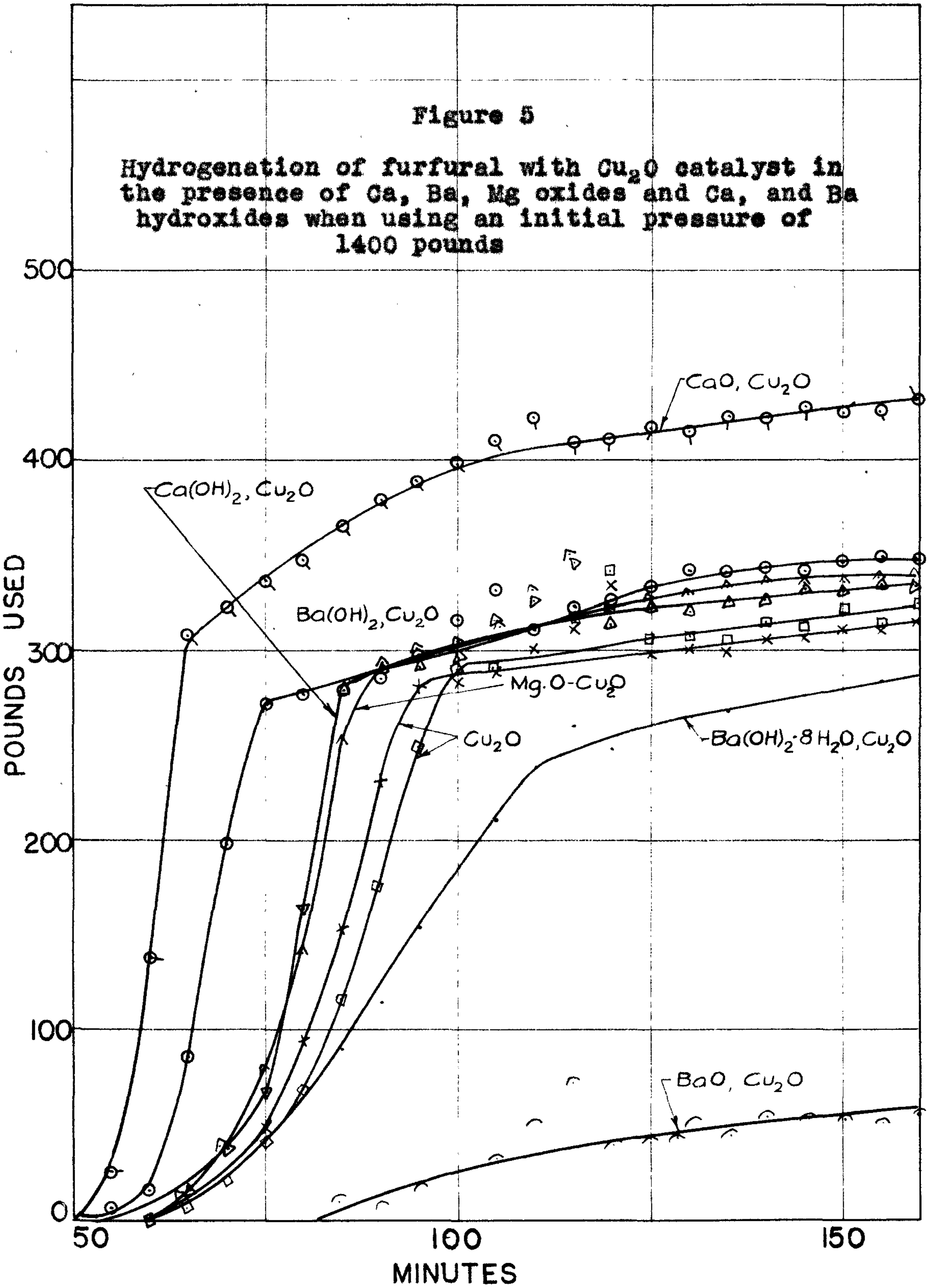
TABLE VI

Results obtained by the addition of the oxides of Ca, Ba, and Mg, and the hydroxides of Ca, and Ba, to Cu_2O catalyst at 1400 lbs. starting pressure

Experiment Number	14c4e	14b4b	14b4a	14a4h	14f4	14a4g	14a4f
Catalyst used, Cu_2O and .089 moles of	CaO	$Ba(OH)_2$	$Ca(OH)_2$	MgO		$Ba(OH)_2 \cdot 8H_2O$	BaO
Reaction starts at °C.	154	164	164	176	161	174	213
Reaction starts at pounds	1915	1985	1990	2015	1965	2060	2205
Per-cent of furfural in the product	2.58	4.00	2.57	4.33	4.79	5.53	67.10
Moles of H_2 used	3.93	3.28	3.09	3.17	2.82	2.49	0.51
Temperature range at greatest pressure drop	177 to 190	194 to 203	215 to 224	215 to 224	227 to 235	230 to 237	?
Pounds of H_2 used during greatest pressure drop	138 to 308 or 170	85 to 198 or 113	165 to 282 or 117	141 to 252 or 111	176 to 250 or 74	115 to 154 or 39	to ?
Temperature at maximum pressure	165	185	196	196	201	214	236
Maximum pressure	1925	2055	2070	2045	2075	2125	2280
Time to react with 2.25 moles of H_2	14	23	28	25	40	57	did not

Figure 5

Hydrogenation of furfural with Cu_2O catalyst in the presence of Ca, Ba, Mg oxides and Ca, and Ba hydroxides when using an initial pressure of 1400 pounds



The two curves labelled Cu_2O in Figure 5 represents two catalysts prepared at different times, by the same method, and show that the activity of the catalyst can be duplicated.

A comparison of the effects of the calcium, barium, and magnesium compounds on the activity of a catalyst, would probably be the most useful if made with an equal number of molecules of the particular compound.

It is apparent that CaO lowers the initial temperature of activation of Cu_2O about 7°, and that $Ba(OH)_2 8H_2O$, MgO, and BaO raise the initial temperature of activation by amounts increasing in the order mentioned. The BaO seems to be very detrimental to the activity of the Cu_2O as a catalyst, since only a small amount of hydrogen reacted.

Calcium oxide enhances the catalytic action of Cu_2O in all of the items taken into consideration in the table. Why BaO, a compound similar to CaO in its chemical properties, should differ so much in its effects on Cu_2O was not determined.

The curves in Figure 5 show that the rate of reaction is greater in the experiment where CaO is used with Cu_2O than in the other experiments. Three moles (334 pounds) of hydrogen are required to convert 3 moles of furfural to furfuryl alcohol. In the experiments where CaO was not used, 334 pounds of hydrogen was not used until at least 25 minutes after the maximum temperature was reached. The maximum temperature was reached in about 100 minutes. In the case where CaO was used, 334 pounds of hydrogen had reacted about 25 minutes before the maximum temperature was reached. The increased rate of hydrogenation, when using CaO with Cu_2O as a catalyst, could be caused by the hydrogenation of the furfuryl alcohol as soon as any alcohol is produced.

In the experiment where Cu_2O-CaO was used, the temperature was 190° at the end of the five minute interval during which the highest rate of reaction occurred. The pounds of hydrogen which had been used by this time were 308, or enough to convert 90% of the furfural to furfuryl alcohol.

Discussion of the results of Table 7 and Figure 6

The amount of catalyst used in the experiments in Table 7 was 8.6 grams. In experiments 14c4e, 14al3a, 14al2e, 5 grams of the compound indicated in the table were added.

When using an initial pressure of 1,400 pounds, the temperature at which reaction starts in the presence of Cu_2O-$Ca(OH)_2$ (co-precipitated), catalyst is 13 degrees below that of the experiment using Cu-Cr oxide (Adkins 30 R.A.C.) catalyst, and 23 degrees below the experiment where Cu-Cr oxide (Calingeart and Edgar) catalyst is used. The pressure at the time reaction starts is much lower in the experiment where the Cu_2O-$Ca(OH)_2$ (co-precipitated) catalyst is used

TABLE VII

Comparative data of the most active catalysts in the Tables V, VI, and some other catalysts when using a pressure of 1400 pounds at the start of the hydrogenations

Experiment Number	14a23	14c4e	14a26	14al2e	14al3a	14b2	14al
Catalyst used	Cu-Cr23	Cu_2O + CaO	Cu_2O $Ca(OH)_2$ copptd	Cu-Crl2 + CaO	CuCrl3 $Ca(OH)_2$	Cu-Cr2	Cu-Crl
Reaction starts at °C.	145	154	132	155	145	146	169
Reaction starts at pounds	1865	1915	1775	1905	1945	1940	2085
Per-cent of furfural in the product	1.3	2.58	2.23	2.39	0.33	1.48	4.93
Moles of H_2 used	4.64	3.93	3.56	3.09	3.99	2.81	2.70
Temperature range at greatest pressure drop	157 to 168	177 to 190	178 to 190	178 to 189	198 to 208	229 to 236	236 to 237
Pounds of H_2 used during greatest pressure drop	29 to 184 or 155	138 to 308 or 170	127 to 260 or 133	50 to 136 or 86	174 to 303 or 129	200 to 250 or 50	108 to 155 or 47
Temperature at maximum pressure	157	165	155	167	178	196	214 +223
Maximum pressure	1870	1925	1835	1930	2055	2125	2240
Time to react with 2.25 moles of H_2	13	14	24	24	28	50	67

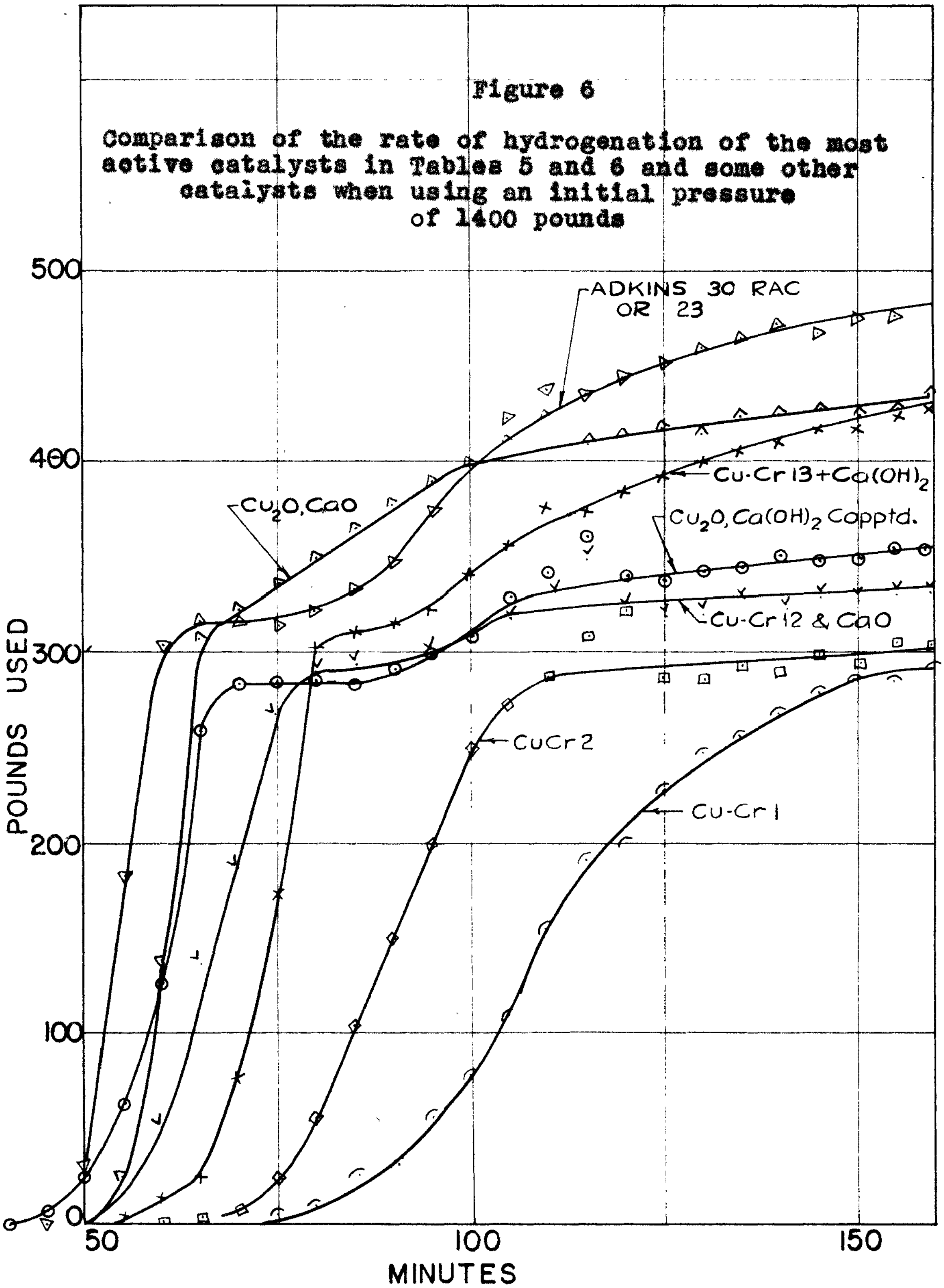


Figure 6

Comparison of the rate of hydrogenation of the most active catalysts in Tables 5 and 6 and some other catalysts when using an initial pressure of 1400 pounds than in the other experiments. The $Cu_2O-Ca(OH)_2$ (co-precipitated) catalyst has interesting possibilities, worthy of more study.

The greatest rate of reaction during any five minute interval, is shown by the Cu_2O, CaO catalyst, which is a drop of 170 pounds in pressure (calculated to 0°C.). This highest rate occurred between the temperatures of 177-190. This highest rate of reaction was over three times as fast as the rate, when using Cu-Cr oxide, catalyst No. 1 or 2, and two times the rate produced when using Cu-Cr oxide, catalyst No. 12 with 5 grams of CaO.

The Cu-Cr oxide, catalyst No. 23 (Adkins 30 R.A.C.) is similar in activity to Cu_2O with CaO, catalyst No. 4e. The time to react with 2.25 moles of hydrogen is about the same in both cases. The temperature at which reaction starts is slightly lower in the case of No. 23, but the maximum rate appears to be slightly greater in the case of catalyst No. 4e.

The Cu-Cr oxide, catalysts No. 1 and 2 are much slower in their action than the other catalysts in Table 7 and Figure 6, and also the total amount of hydrogen used is less than in the other cases.

Discussion of the results of Table 8 and Figure 7

The catalyst used in the experiments reported in

Table 8 was 8.6 grams of Cu_2O and 5 grams (0.089 moles) of CaO.

An inspection of the table shows that the temperature at which reaction starts is independent of the pressure.

The curves in Figure 7 show about the same rate of reaction below the point where 300 pounds of hydrogen has been used for initial pressures of 1,000 and 1,900 pounds, but the rate of reaction appears to be increased more by pressure after 300 pounds of hydrogen has reacted as is shown by the increasing divergence of the lines as the pressure is increased.

The greatest rate of reaction occurs between the temperatures of 158 to 190 at initial pressures of 1,000 to 1,900 pounds. The pounds of hydrogen that reacted during the five minute interval of greatest reaction, increases with pressure up to 1,400 pounds.

The product (983.2 grams), from four of the hydrogenations of furfural, when using Cu_2O-CaO catalyst at an initial pressure of 1,400 pounds, was combined and distilled at atmospheric pressure until the thermometer reached 150°C. The distillate was fractionally distilled, and gave 14 ml. of water, and 13.4 grams (1.36%) of 2-methylfuran (sylvan) after drying over $CaCl_2$ and redistilling. The sylvan was identified by the following: b.p. 63-64° (737.1mm), d_4^{20} .914, n_D^{24} 1.4322 5-methyl-2-chloromercurifuran

TABLE VIII

Results obtained in the hydrogenations of furfural at different pressures with Cu_2O and CaO, catalyst number 4e

Experiment Number	19a42	14c4e	12b4e	10a4e	6a4e	4a4e
Pressure used at the start	1900	1400	1200	1000	600	400
Reaction starts at °C	146	154	150	155	153	162
Reaction starts at pounds	2625	1915	1660	1350	815	565
Per-cent of furfural in the product	4.96	2.58	4.08	3.57	3.17	2.22
Moles of H_2 used	4.32	3.93	3.24	3.62	3.1	2.87
Temperature range at greatest pressure drop	158 to 169	177 to 190	173 to 183	177 to 189	197 to 208	194 to 204
Pounds of H_2 used during greatest pressure drop	21 to 183 or 162	138 to 308 or 170	73 to 216 or 143	88 to 216 or 128	174 to 278 or 104	106 to 169 or 63
Temperature at maximum pressure	158	165	162	165	164	162
Maximum pressure	2665	1925	1690	1365	835	565
Time to react with 2.25 moles of H_2	12.5	13	16	16	24	63

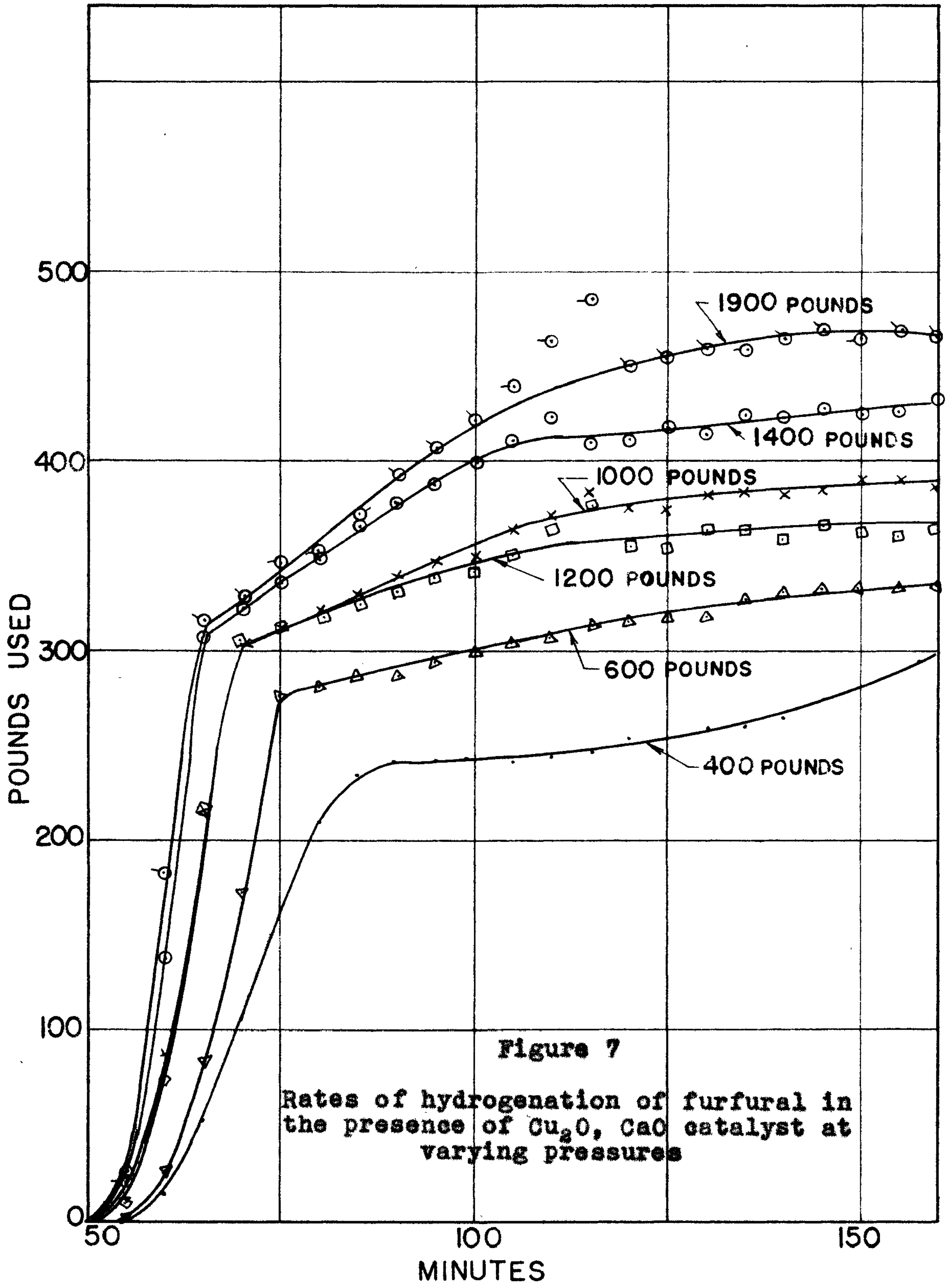


Figure 7

Rates of hydrogenation of furfural in the presence of Cu_2O, CaO catalyst at varying pressures derivative (18)(31) m.p. 133°.

The residue (above 150°) produced by fractional distillation, 764.5 grams (77.8%) of furfuryl alcohol with a boiling point of 74-75 at 17 mm. The alcohol was identified by the formation of the α-naphthyl urethane (4) derivative which had a melting point of 129.5°C.

The liquid boiling at a higher temperature than furfuryl alcohol was not investigated.

Discussion of the results of Table 9 and Figure 8

The amount of catalyst used in each of the experiments in Table 9 was 8.6 grams. In the experiments whose numbers end with 4e, 5 grams of CaO were added.

Copper-chromium oxide, catalyst No. 23 was one of the better catalysts (30 R.A.C.) reported by Adkins and his students.

The activity of catalyst No. 23 is very similar to that of Cu_2O-CaO, catalyst No. 4e. The temperature at which reaction starts is slightly lower in the case of No. 23 than in No. 4e at initial pressures of 1,900, 1,400, and 600 pounds. Although the reaction starts at a lower temperature when using Cu-Cr oxide, catalyst No. 23, it does not produce as rapid a decrease in pressure during the five minute interval of maximum pressure drop, as does the Cu_2O, CaO, catalyst No. 4e.

TABLE IX

Comparison of the activity of Cu_2O, CaO catalyst number 4e, with Adkins catalyst 30 RAC

Experiment Number	19a23	19a4e	14a23	14c4e	6a23	6a4e
Catalyst used	Cu-Cr23	Cu-Ca4e	Cu-Cr23	CuCa4e	Cu-Cr23	CuCa4e
Pounds used at the start	1900	1900	1400	1400	600	600
Reaction starts at °C.	122	146	145	154	122	153
Reaction starts at pounds	2460	2625	1865	1915	775	815
Per-cent of furfural in the product	2.02	4.96	1.3	2.58	2.02	3.17
Moles of H_2 used	5.27	4.32	4.64	3.93	3.45	3.1
Temperature range at greatest pressure drop	157 to 169	158 to 169	157 to 168	177 to 190	167 to 179	197 to 208
Pounds of H_2 used during greatest pressure drop	124 to 264 or 140	21 to 183 or 162	29 to 184 or 155	138 to 308 or 170	99 to 195 or 96	174 to 278 or 104
Temperature at maximum pressure	145	158	157	165	155	164
Maximum pressure	2590	2665	1870	1925	830	835
Time to react with 2.25 moles of H_2	17.5	12.5	13	14	29	24

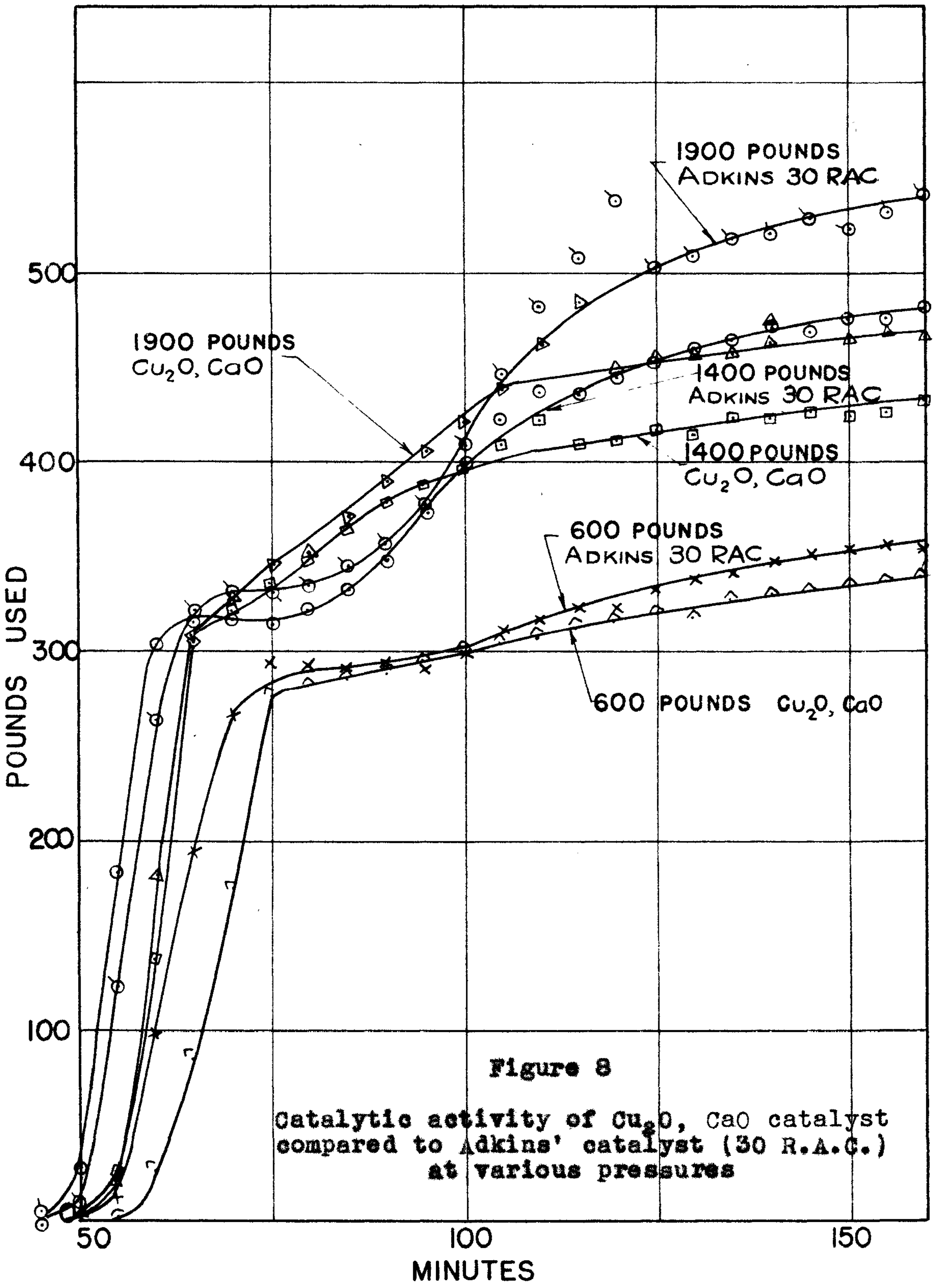


Figure 8

Catalytic activity of Cu_2O, CaO catalyst compared to Adkins' catalyst (30 R.A.C.) at various pressures

In Figure 8 the similarities of the two catalysts are easily seen at 600 and 1,400 pounds of initial pressures.

The curves for 1,900 pounds show a slightly greater increase in rate, for Cu-Cr oxide, catalyst No. 23 than for the Cu_2O, CaO catalyst, after 100 minutes of reaction. The bomb reaches its maximum in about 100 minutes. Cu-Cr oxide, No. 23 appears to be slightly more active in the hydrogenation of furfuryl alcohol when the bomb is cooling than Cu-Cr oxide, catalyst No. 4e.

Since the two catalysts are so similar in their activity, it is possible that the only part that the chromium plays in the copper-chromium oxide catalysts, is that of an inert carrier, which prevents sintering in the preparation of the catalyst. Aluminum oxide has been reported to play the role of promoter by the prevention of sintering in the case of NiO catalysts (6).

Catalyst No. 4e was not prepared by co-precipitating the calcium and copper together, but by adding the 0.089 moles of CaO to the Cu_2O after the Cu_2O was prepared.

Catalysts formed by co-precipitation are more active than those produced by mixing the compounds (14). It seems very probable that a catalyst could be prepared by co-precipitation of Cu_2O and $Ca(OH)_2$ which would be more active than those yet studied.

The Cu_2O-$Ca(OH)_2$ catalyst, formed by co-precipitation, and used in experiment No. 14a26 of Table 7, shows initial reaction at 132°, whereas Cu-Cr oxide, catalyst No. 23 in experiment No. 14a23 of Table 9 shows initial reaction at 145°. The reaction does not go as far in the experiment where Cu_2O-$Ca(OH)_2$ (co-precipitated) was used because only 3.56 moles of hydrogen were used, while in the experiment where Cu-Cr oxide, catalyst No. 23 was used, 4.64 moles of hydrogen were used.

The number of moles of calcium used in the preparation of Cu_2O-$Ca(OH)_2$ (co-precipitated), catalyst No. 26 was 0.266 with 0.413 moles of copper, whereas, in the Cu-Cr oxide, catalyst No. 23, 0.0206 moles of barium were used with 0.413 moles of copper. Smaller amounts of calcium than that used in catalyst No. 26 might produce a much better catalyst.

<u>Discussion of the results reported in Table 10</u>

In each of the experiments reported in Table 10, 8.6 grams of catalyst were used with 250 ml. of furfural.

The Cu_2O catalyst is of special interest as Cu_2O with Cr_2O_3 has been reported to produce no reaction of hydrogen with acetone at 200°C. and 150-250 atmospheres (14).

Apparently the method of preparing Cu_2O has a decided effect on its activity, as Cu_2O (C.P.) from Baker and Adamson showed no activity at an initial pressure of 1,400 pounds and a temperature up to 237°C., neither did

TABLE X

Catalysts which were observed to have little or no Activity at 1400 pounds pressure

Catalyst	Pounds of H_2 used calculated to 0°C	Product	% Furfural
Cu_2H_2	None	Black, polymerized solid	
Cu (pptd) J. T. Baker Chemical Co.	None	Some polymerization	Not analyzed
CuO (powder) Cu_2O	240	Two layers formed H_2O and condensation product	Not analyzed
Cu_2O, C.P. (Baker and Adamson)	None	Some polymerization	81.00
Cu_2O (prepared by reduction with SO_2)	25	Some polymerization	79.75
Cu, Ur oxides	161	Some polymerization	38.14
Cr_2O_3	125	Some polymerization	52.30
NiO (green)(Sargeant & Co.)	14	Some polymerization	78.93

Cu_2O prepared by reduction with SO_2, whereas Cu_2O prepared by reduction with dextrose produced rapid hydrogenation as has already been shown in Tables 6, 7, 8, and 9.

CONCLUSIONS

1. For any one catalyst the temperature at which hydrogenation starts is independent of the initial pressure of hydrogen between 200 and 1,800 pounds.

2. The temperature, at which hydrogenation starts is different for different catalysts when using the same pressures.

3. The lowest temperature at which hydrogenation starts, with any catalyst used in this study, was 122°, when using Cu-Cr oxide, catalyst No. 23, at initial pressures of 600 and 1,400 pounds.

4. The lowest temperature, at the beginning of the five minute interval, during which the greatest rate of reaction took place, was 157°, when using Cu-Cr oxide No. 23 at initial pressures of 1,400 and 1,900 pounds. However, Cu_2O, CaO catalyst No. 4e had a temperature of 158° at the beginning of the five minute interval, for its greatest rate of reaction when using an initial pressure of 1,900 pounds.

5. The greatest drop in pressure (calculated to 0°) during any five minute interval was 170 pounds and was produced by Cu_2O, CaO, catalyst No. 4e, at an initial pressure of 1,400 pounds.

6. The Cu-Cr oxide, catalyst No. 23, caused the greatest total amount of hydrogen to react (5.27 moles) when using an initial pressure of 1,900 pounds.

7. Copper oxide, calcium oxide, catalyst No. 4e, caused 2.25 moles of hydrogen to react in the least number of minutes (12.5) when the initial pressure was 1,900 pounds.

8. The Cu_2O, CaO mixture is a good catalyst for the hydrogenation of furfural and is much easier and simpler to prepare than the Cu-Cr oxide catalysts.

9. The only advantage of using more than 1,000 pounds of initial pressure, in the hydrogenation of furfural to furfuryl alcohol, is a slight increase in the rate of reaction.

SUMMARY

1. The hydrogenation of furfural in the liquid phase at initial pressures from 200 to 1,900 pounds and temperatures up to 237°C. in the presence of Cu_2O, and several Cu-Cr oxide catalysts, and modifications of these, by the use of the oxides of calcium, barium, and magnesium and of the hydroxides of calcium and barium, was investigated in a rocking type, copper lined, autoclave of approximately 3 feet in length and an inside diameter of about 3 inches, and having a capacity of nearly 3.85 liters.

2. Pressure has more effect on the hydrogenation of furfural, in the presence of a Cu-Cr oxide catalyst, at initial pressures of 200 to 600 pounds, than from 600 to 1,800 pounds.

3. In the hydrogenation of furfural at an initial pressure of 1,400 pounds, CaO, $Ca(OH)_2$, $Ba(OH)_2$ enhance (in the order mentioned) the activity of Cu-Cr oxide, but CaO decidedly more than the others. $Ba(OH)_2 \cdot 8H_2O$ is much more detrimental to the catalytic action of Cu-Cr oxide than BaO.

4. In the hydrogenation of furfural at an initial pressure of 1,400 pounds, CaO, $Ba(OH)_2$, $Ca(OH)_2$, and MgO

enhance (in the order mentioned) the catalytic activity of Cu_2O, but CaO decidedly more than the others. BaO is much more detrimental to the catalytic action of Cu_2O than $Ba(OH)_2 \cdot 8H_2O$.

5. The activity of five Cu-Cr oxide catalysts*, Cu2O, Cu_2O mixed with CaO, and a Cu_2O with $Ca(OH)_2$ (co-precipitated) were compared in their rates of hydrogenation of furfural at 1,400 pounds of initial pressure and temperatures up to 237°C. The Cu_2O with CaO catalyst produced the greatest rate of reaction.

6. Pressure has more effect on the hydrogenation of furfural, in the presence of Cu_2O with CaO catalyst, at initial pressures of 400 to 1,000 pounds, than from 1,000 to 1,900 pounds.

7. The activity of Cu-Cr oxide catalyst (Adkins 30 R.A.C.) was compared with a Cu_2O CaO catalyst, at initial pressures of 600, 1,400, and 1,900 pounds, and temperatures up to 237°C. The two catalysts were found to be very similar.

8. The method of preparing the Cu_2O catalyst is very vital to its activity.

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* Includes Adkins (30 R.A.C.) and Calingaert and Edgar's catalysts.

LITERATURE CITED

1. Adkins, H. and Connor, R. The catalytic hydrogenation of organic compounds over copper chromite. J. Am. Chem. Soc. 53:1091-1095. 1931.

2. Adkins, H., Folkers, K. and Kinsey, M. The reactions of acetaldehyde over zinc chromite under a pressure of 210 atmospheres. J. Am. Chem. Soc. 53:2714-2720. 1931.

3. Adkins, H., Kommes, C. E., Struss, E. F. and Dasler, W. The preparation of aldehydes and ketones by dehydrogenation of alcohols over copper-chromium oxide. J. Am. Chem. Soc. 55:2992-2994. 1933.

4. Bickel, V. T. and French, H. E. Alpha-naphthylisocyanate as a reagent for alcohols. J. Am. Chem. Soc. 48:747-751. 1926.

5. Bourguignon, A. Hydrogénation du furfurane. Bull. Soc. chim. Belg. 22:87-93. 1908.

6. Boswell, M. C. and Iler, R. K. Nickel catalysts. I The effect of the temperature of preparation on the crystal size and composition of nickel oxide. J. Am. Chem. Soc. 58:924-928. 1936.

7. Bouveault, L. Sur la transformation des alcools primaires en aldehydes et hydrogène. Bull. soc. chim., [4] 3:119-124. 1908.

8. Brown, F. E., Gilman, H. and Van Peursem, R. Hydrogenation of furfural. Iowa State Coll. J. Sci. 6:133-136. 1932.

9. Burdick, H. E. and Adkins, H. Hydrogenation and hydrogenolysis of furan derivatives. J. Am. Chem. Soc. 56:438-442. 1934.

10. Calingaert, G. and Edgar, G. Small-plant-scale liquid-phase hydrogenation under high pressure. Ind. Eng. Chem. 26:878-880. 1934.

11. Conant, J. B., Webb, C. N. and Mendum, W. C.

Trimethylacetaldehyde and dimethylacetaldehyde. J. Am. Chem. Soc. 51:1246-1255. 1929.

12. Connor, R. and Adkins, H. Hydrogenolysis of oxygenated organic compounds. J. Am. Chem. Soc. 54:4678-4690. 1932.

13. Connor, R., Folkers, K. and Adkins, H. The preparation of copper-chromium oxide catalysts for hydrogenation. J. Am. Chem. Soc. 53:2012. 1931.

14. Connor, R., Folkers, K. and Adkins, H. The preparation of copper-chromium oxide catalysts for hydrogenation. J. Am. Chem. Soc. 54:1138-1145. 1932.

15. Corenwinder, M. B. Sur la production directe des hydracides, a l'aide des corps poreux. Ann. Chim. Phys. (3) 34:77-81. 1852.

16. Covert, L. W., Connor, R. and Adkins, H. The use of nickel as a catalyst for hydrogenation. II. J. Am. Chem. Soc. 54:1651-1663. 1932.

17. Debus, H. Ueber die Darstellung des Methylamines aus Blausäure und Wasserstoff. Ann. 128:200-215. 1863.

18. Gilman, H. and Wright, G. Furan mecurials. J. Am. Chem. Soc. 55:3302-3314. 1933.

19. Jolles, A. Über ein neues Verfahren zur quantitativen Bestimmung der Pentosen. Z. für Anal. Chem. 45:196-204. 1906.

20. Kaufmann, W. E. with Adams, R. The use of platinum oxide as a catalyst in the reduction of organic compounds. IV. The reduction of furfural and its derivatives. J. Am. Chem. Soc. 45:3029-3044. 1923.

21. Kolthoff , I. M., Menzel, I. H. and Furman, N. H. The theoretical principles of volumetric analysis. I: p. 186. John Wiley and Sons, Inc., New York. 1929.

22. Kolthoff, I. M., Menzel, I. H. and Furman, N. H. Practical volumetric analysis II: p. 451. John Wiley and Sons, Inc., New York. 1929.

23. Komatsu, S. and Masumoto, M. Studies on catalytic action at high pressure and temperature. Bull. Chem. Soc. Japan 5:244-248. 1930.

24. Kotake, M. and Funita, Y. Reduction of furfural in the presence of nickel catalyst. (Trans. title) J. Chem. Soc. Japan. 51:354-356. 1930. Original not seen. C. A. 25:3649. 1931.

25. Kuhlmann, F. Sur plusieurs réactions nouvelles dèterminées par l éponge de platine, et considerations sur les services que cette substance est appelée à rendre à la science. Compt. Rend. 7:1107-1110. 1838.

26. Mellor, J. W. A comprehensive treatise on inorganic and theoretical chemistry. Vol. 3. p. 119. Longmans Green and Co., London. 1923.

27. Miller, P. The free energy of furfural and some of its derivatives. Unpublished thesis. Library, Iowa State College, Ames, Iowa. 1929.

28. Minne, N. and Adkins, H. Structure of reactants and the extent of acetal formation. J. Am. Chem. Soc. 55:299-309. 1933.

29. Padoa, M. e Ponti, U. Sulla riduzione del nucleo furanico. Atti accad. Lincei. [5] 15. II 610-615. 1906. Original not seen. Abstracted in Chem. Zentr. 78:570. 1907.

30. Parkinson, A. E. and Wagner, E. C. Estimation of aldehydes by the bisulfite method. Ind. Eng. Chem. Anal. Ed. 6:433-436. 1934.

31. Paul, R. Phénomenes d'oxydo-réduction observés dans la deshydration d'alcools à noyau furanique. Bull. soc. chim. [5] 2:2220-2224. 1935.

32. Piccard, J. and Thomas, E. Metaux catalytiques. Helv. Chim. Acta 6:1044-1045. 1923.

33. Pringsheim, H. and Noth, H. Üeber Versuche zur katalytischen Reduktion des Furfurols. Ber. 53:114-118. 1920.

34. Roberti, Giorgio. L'idrogenazione del furfurolo. Ann. Chim. applicata 25:530-540. 1935.

35. Sarma, V. V. Cuprous oxides by reduction. Chem. News 122:99-100. 1921.

36. Scheibler, H., Sotscheck, F. and Friese, H. Über

Tetrahydrofurfuryl alcohol. Ber. 57:1443-1448. 1924.

37. Schmidt, Otto. The mechanism of heterogenous catalytic organic reactions. I. Catalytic hydrogenation. Chem. Rev. 12:363-417. 1933.

38. Starr, D. and Hixon, R. M. Reduction of furan and the preparation of tetramethylene derivatives. J. Am. Chem. Soc. 56:1595-1596. 1934.

39. von Wilde, M. P. Einwirkung des Wasserstoffs auf das Acetylen und Aethylen in Berührung mit Platinschwarz. Ber. 7:353-355. 1874.

40. Vorlander, D. and Meyer, F. Einwirkung von Kupferwasserstoff auf o-Diazobenzöesäure. Ann. 320:143-144. 1902.

41. Weston, P. E. and Adkins, H. Catalysis in the conversion of allyl alcohol and acrolein into propionaldehyde. J. Am. Chem. Soc. 50:1930-1935. 1928.

42. Wienhaus, H. Hydrierung des Furfuralkohols und des Furfurols zu Tetrahydrofurfuralkohol. Ber. 53: (II) 1656-1666. 1920.

43. Wojcik, B. and Adkins, H. Hydrogenolysis of alcohols to hydrocarbons. J. Am. Chem. Soc. 55:1293-1294. 1933.

44. Zelinski, N. D. and Schuikin, N. I. Nuclear hydrogenation of furan with osmium catalyst. (Trans. title) Compt. rend. acad. sci. U. R. S. S. (n.s.) 1933. 60-3. (in German 64-5). Original not seen. C. A. 28:2002. 1934.