TABLE I. DISTRIBUTION COEFFICIENTS

V = H_2S content of gas, %
H = average H_2S content of hydrocarbon, g./g.
W = average H_2S content of water, g./g.
D = maximum deviation from average, %
K = distribution ratio, H/W

	Run	V	H	D	W	D	K
Benzene 25° C.	0.9	100	0.01088	1.9	0.00165	0.9	6.6
	0.10	56	0.0092	0.5	0.00142	3.5	6.5
	0.11	56	0.00882	...	0.001325	...	6.65
	0.12	56	0.0088	1.1	0.00134	1.9	6.55
	0.13	35	0.00681	0.6	0.000978	0.9	6.96
						Av.	6.65
Gasoline 15° C.	1.4	100	0.0137	9.5	0.002193	0.2	6.25
	1.5	100	0.0117	3.4	0.00225	3.6	5.2
	1.6–9	100	0.0136	2.9	0.0021	1.7	6.5
						Av.	5.65
25° C.	1.2	100	0.0127	3.9	0.00198	1.5	6.4
	1.3	100	0.0127	8.7	0.002083	8.1	6.1
	1.18	35	0.00416	2.9	0.00066	8.6	6.3
						Av.	6.30
35° C.	1.7	100	0.00891	...	0.001271	...	7.0
Kerosene 15° C.	2.1	100	0.00662	9.2	0.001815	3.3	3.65
25° C.	2.3	100	0.00623	3.1	0.00207	0.2	3.0
	2.5	56	0.0049	4.7	0.001493	1.3	3.3
	2.6	56	0.00486	5.1	0.00157	5.7	3.1
						Av.	3.20
35° C.	2.4	100	0.00526	1.7	0.001665	2.1	3.2

TABLE II. WATER REQUIREMENT AND THEORETICAL PLATES FOR COUNTERCURRENT EXTRACTION AT 25° C.

K = average distribution ratio
W = lb. water/lb. hydrocarbon
w = gallons water per gallon hydrocarbon
X_1 = lb. H_2S/lb. hydrocarbon leaving tower
X_2 = lb. H_2S/lb. hydrocarbon entering tower, 0.005
Y_1 = lb. H_2S/lb. water entering tower, 0.00
Y_2 = lb. H_2S/lb. water leaving tower
n = number of theoretical plates required in tower

Hydrocarbon	K	W	w	X_1	Y_2	n
Benzene	6.65	5.31	4.75	0.001	0.000752	∞
		6.16	5.50	0.001	0.000650	6
		6.71	6.00	0.001	0.000596	5
		7.84	7.00	0.001	0.000510	3
		6.52	5.83	0.0001	0.000752	∞
		7.84	7.00	0.0001	0.000625	13
		8.94	8.00	0.0001	0.000548	8
		10.08	9.00	0.0001	0.000486	6
Gasoline	6.3	5.04	3.7	0.001	0.000793	∞
		5.85	4.25	0.001	0.000684	6
		6.20	4.50	0.001	0.000645	5
		6.88	5.00	0.001	0.000581	4
		6.18	4.50	0.0001	0.000793	∞
		6.88	5.00	0.0001	0.000713	21
		7.56	5.5	0.0001	0.000649	13
		8.26	6.0	0.0001	0.000593	9
Kerosene	3.2	2.50	2.00	0.001	0.00160	∞
		2.75	2.20	0.001	0.00146	8
		3.38	2.70	0.001	0.00118	4
		3.75	3.00	0.001	0.00107	3
		2.50	2.00	0.0001	0.00160	∞
		3.75	3.00	0.0001	0.00131	13
		4.37	3.50	0.0001	0.00112	8
		5.00	4.00	0.0001	0.00096	6

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Vapor Phase Hydrogenation of Furfural to Furfuryl Alcohol

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RECENTLY the vapor phase hydrogenation of furfural to 2-methylfuran was studied in these laboratories (*4*). After the chromite catalyst had been in use for several days it was noted that measurable quantities of furfuryl alcohol were produced. However, the catalyst was losing its activity and the yield of both 2-methylfuran and furfuryl alcohol rapidly decreased. This manuscript reports the conditions for the production of high yields of furfuryl alcohol with the same type catalyst.

A number of vapor phase hydrogenations of furfural to furfuryl alcohol have been reported (*3, 10, 12–14*). In general these procedures either required more than one pass for complete conversion of the furfural or a variety of products was obtained. The presence of considerable quantities of 2-methylfuran, tetrahydrofurfuryl alcohol, and the several pentanediols is due to the use of a nonselective catalyst—e.g., nickel—and/or rather high reaction temperatures.

Several reported liquid phase hydrogenations of furfural have given good yields of furfuryl alcohol (*2, 5, 7–9, 11*). Commercial production of furfuryl alcohol is at present based on the use of a high pressure batch process. A continuous atmospheric pressure procedure offers several obvious economic advantages over the high pressure batch process.

MATERIALS

Technical grade furfural was obtained through the courtesy of The Quaker Oats Company. A middle fraction from the distillation at reduced pressure in a nitrogen atmosphere was used for this investigation. Chemicals used in the preparation of the copper chromite catalyst were reagent grade purchased from the General

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A procedure for the continuous vapor phase hydrogenation of furfural to furfuryl alcohol is reported. The method involves passing the mixed vapors of hydrogen and furfural at atmospheric pressure over a calcium-stabilized copper chromite catalyst at 100° to 140° C. Yields of water-white furfuryl alcohol up to 95% are recovered after one pass. 2-Methylfuran is the principal by-product, the yield of this material increasing with an increase in the reaction temperature. On a laboratory scale the catalyst was still active after 68 grams of furfural had been hydrogenated for each gram of catalyst used. The process should be adaptable to commercial production of furfuryl alcohol.

Chemical Company. The charcoal used as a catalyst support was 4- to 10-mesh Norit A (American Norit Company) or Nuchar (West Virginia Pulp & Paper Company). Glass beads also used as a catalyst support were smooth, Kimble brand, 6-mm. size beads.

PREPARATION OF THE CATALYST

The calcium-stabilized copper chromite catalyst was prepared by the procedure described by Holdren (*4*) in connection with the production of 2-methylfuran. This method combines several previously described modifications of the Adkins catalyst (*1*). Precipitation of the complex chromates from a neutral solution and decomposition in small quantities at a controlled temperature (about 300° C.) enhanced the catalyst activity. In early studies on the production of furfuryl alcohol the activity of the catalyst was estimated by the yield of 2-methylfuran produced under the optimum conditions described by Holdren (*4*). This gave a method for testing the uniformity of various catalyst preparations.

In a typical preparation 522 grams of copper nitrate trihydrate and 62 grams of calcium nitrate tetrahydrate in 1800 ml. of aqueous solutions were heated to 80° C. and then added to 1800 ml. of a solution containing 302 grams of ammonium dichromate and sufficient concentrated ammonium hydroxide to leave the mother liquor at a pH 7 (400 ml. of the base were required for this experiment). The suspension was stirred vigorously until it had cooled to room temperature and then filtered. After drying at 75° C. for 30 hours the complex chromates were pulverized and decomposed in a small rotary kiln at about 300° C. (temperature reading is that taken from a thermometer, the bulb of which is placed in the catalyst at the point of most vigorous decomposition). Fifty-gram batches of the light brown material were then heated in an air bath until the temperature in the sample rose to 200° C. Leaching with 10% acetic acid, washing with water, and drying at 105° C. gave 288 grams of catalyst.

The pulverized catalyst was deposited on the wet charcoal or wet glass beads as a carrier and dried in a hydrogen atmosphere. When charcoal was the carrier, the weight ratio of catalyst to carrier was 1.5 to 1. For the glass beads the same weight of catalyst was used for a given bed depth as with the charcoal. This gave a weight ratio of about 0.13 to 1 for catalyst to beads. Because only the exposed surface is effective, smaller quantities of catalyst would probably suffice.

APPARATUS AND PROCEDURE

A sketch of the all-glass apparatus used for this investigation is shown in Figure 1. The feed unit made use of a 10 r.p.m. synchronous motor which through a series of changeable gears drove the ground-glass plunger of a 50-ml. injection syringe downward at a constant rate. Furfural was fed from the hypodermic needle into the vaporizer which was filled with glass wool and electrically heated to 150° to 160° C. From the vaporizer furfural vapor and hydrogen gas were led directly into the top of the reaction tube. A small electric furnace served to heat the reaction chamber. Two thermometers, identified as heavy black lines in Figure 1, gave the temperature at the top and bottom of

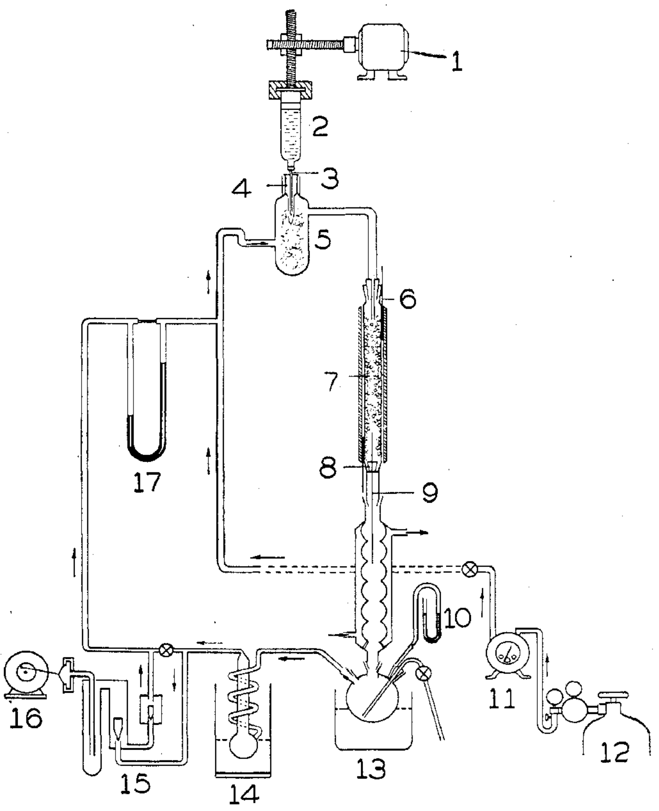

Figure 1. Laboratory Hydrogenation Apparatus

1. Motor for driving syringe plunger
2. Glass syringe
3. Hypodermic needle
4. Rubber stopple
5. Vaporizer
6. Furnace thermometer
7. Catalyst bed
8. Notched cork supporting catalyst thermometer
9. Catalyst thermometer
10. Manometer
11. Precision gas meter
12. Hydrogen supply tank
13. Ice-salt bath
14. Dry ice-acetone bath
15. Glass check valves
16. Diaphragm pump
17. Gas flowmeter

Table I. Vapor Phase Hydrogenation of Furfural

No.	Feed Rate, G./Hr.	Contact Time, Sec.	Mole Ratio, Hydrogen to Furfural	Catalyst Bed Temp. (Center), ° C.	% Furfural Recovered after Distillation as		
					Unreacted furfural	2-Methylfuran	Furfuryl alcohol
			A. Copper Chromite Catalyst Supported on Charcoal				
A-2	25	0.5	39:1	188–92	0.8	53.9	26.6
A-3	20	0.8	32:1	169–72	6.4	1	72
B-2	12.5	0.6	51:1	168–70	1	12.9	65.6
B-3	14.3	0.4	65:1	168–72	6.4	11.7	62.4
C-1	9.1	0.2	107:1	160–2	0.5	14	66.5
C-3	8.4	0.4	61:1	155–61	25.0	4.7	59.6
C-5	13.3	0.2	73:1	178–84	16.9	6.4	53.8
D-2	9.3	1.1	105:1	137–43	0	11.5	82.6
D-3	10.0	1.7	64:1	128–31	2.5	3.8	77.8
E-3	13.6	1.5	71:1	112–5	4.8	0.5	86.4
E-5	16.7	1.5	58:1	126–31	8.0	0.4	82.4
			B. Copper Chromite Catalyst Supported on Glass Beads				
F-2	12.6	1.4	77:1	118–20	1	1	90.1
F-3	23.1	1.4	42:1	120–5	0	1	92.1
F-5	23.4	2.9	20:1	120–30	0	15.4	76.5
F-6	23.1	2.9	20:1	105–9	1	1.2	92.2
F-8	12.8	4.3	25:1	98–101	0	1	91.2
H-2	23.1	1.1	49:1	129–33	0	4.7	89.2
I-2[a]	23.1	1.7	39.4:1	144–6	0	4.7	92.0
J-4	23.1	1.1	39.4:1	130	0.9	0.7	93
J-5	23.1	1.1	39.4:1	137	0	1.9	91.2

[a] This sample of catalyst did not contain the calcium stabilizer. Note the somewhat higher temperature needed for complete conversion of the furfural.

the furnace. A third thermometer supported by a notched cork extended from the upper part of the water condenser into the interior of the catalyst bed. From the reaction tube the products were led through the condenser and the dry ice trap. Recirculation of the hydrogen gas was effected by the use of a diaphragm pump and a pair of ground-glass check valves. The system was maintained at atmospheric pressure (±1 cm.) by regulation of the Hoke valve on the hydrogen supply tank.

Difference in the readings taken from the Precision wet test meter gave the hydrogen consumption. Contact time for the vapor was estimated from the void space in the catalyst bed and the average gas circulation rate for a given run. Hydrogen to furfural ratios (moles per hour) were varied by changing either the feed rate or the hydrogen circulation. Using a given set of calibrated gears on the feed unit the gas circulation rate was set at the value calculated to give the desired mole ratio of hydrogen to furfural.

At the end of an experiment the product was siphoned off and combined with the material collected in the dry ice trap. The 2-methylfuran fraction was first separated by distillation of the wet product through a Claisen head. Then the furfural–furfuryl alcohol fraction was distilled through a 42-cm. Vigreux column in a nitrogen atmosphere at reduced pressure. From the refractive index of the weighed fraction the per cent furfural was calculated (*6*), and the furfuryl alcohol was obtained by difference (the furfuryl alcohol was identified by conversion to the α-naphthylurethane, melting point, 129° C., uncorrected). Mechanical losses amounted to 5 to 6% on a 50-gram sample; the reported yields of furfuryl alcohol are not corrected for this constant loss.

EXPERIMENTAL

In the early experiments charcoal was used as the catalyst support, and the furfural was vaporized from a column of glass beads placed directly above the catalyst in the reaction tube. The use of charcoal as a carrier resulted in the formation of larger proportions of 2-methylfuran than when glass beads were the carrier used. Decreasing the length of the catalyst bed and the contact time gave somewhat lower yields of 2-methylfuran but resulted in incomplete conversion of the furfural. The higher yields of 2-methylfuran may be partially accounted for by the greater surface area exposed and the lower heat capacity of the charcoal which results in a much higher surface temperature than that encountered with the glass beads. Over-all recovery was also lower with the charcoal carrier (compare Table I, A and B). The high vapor pressure of 2-methylfuran and the absorption and/or resinification in the catalyst tube increased the mechanical losses when appreciable quantities of the hydrocarbon were involved. Yields of 2-methylfuran shown in Table I, A, are "in hand" values and the actual amounts formed may have been considerably higher. A few typical experiments with the charcoal-supported catalyst are shown in Table I, A.

Using glass beads as a catalyst support was found to have several advantages over the charcoal—e.g., better heat conduction, less holdup of materials within the bed, easier separation of catalyst from carrier for regeneration or recovery, and less possibility of introducing catalyst poisons. Contact time, feed rate, and ratio of hydrogen to furfural proved to be much less critical when the reaction temperature was kept below 140° C. Table I, B, summarizes the data obtained in typical experiments with the catalyst supported on glass beads.

REACTION TEMPERATURE

Of the several variables considered in this study the reaction temperature seemed to be the most critical. In order to minimize over-heating of the catalyst surface it was necessary to use catalyst bed temperatures below 150° C. and a nonporous carrier such as glass beads. Temperature surges up to 50° C. were noted in the center of a catalyst bed when furfural was added to a fresh charcoal-supported catalyst previously heated at 165° C. in a hydrogen gas stream. Such temperature surges are indicative of much higher increases on the catalyst surface near the top of the bed. With a charcoal carrier and reaction temperatures above 150° C. it was very difficult if not impossible to find a contact time sufficiently long to allow for complete conversion of the furfural and at the same time prevent the formation of 2-methylfuran in quantities less than 10%. This localized overheating of the catalyst surface also tended to decrease the life and activity of a given catalyst sample.

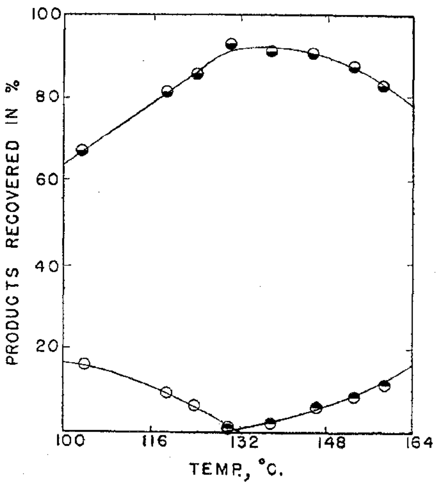

Figure 2. Relationship between Temperature and Degree of Hydrogenation of Furfural

◒ Furfuryl alcohol
○ Furfural
◓ 2-Methylfuran

In order to get a more nearly quantitative measure of the effect of temperature on the course of the reaction a fresh catalyst sample was used to hydrogenate eight 50-gram samples of freshly distilled furfural. All other variables were held constant while the temperature in the center of the catalyst bed was successively raised for each sample of furfural. The operation of the unit was interrupted between samples only long enough to remove the products of the previous run and to establish equilibrium conditions for the next experiment.

In this series the furfural feed rate was set at 23.1 grams per hour, the contact time at 1.2 seconds, the mole ratio of hydrogen to furfural 39.4 to 1, while the reaction temperature was varied from 103° to 158° C. Figure 2 indicates the rather marked effect of temperature on the degree of hydrogenation of the aldehyde group in furfural. Unreacted furfural is recovered in decreasing amounts up to about 130° C. (Figure 2). From this point an increase in reaction temperature results in the formation of increasing quantities of 2-methylfuran (with a corresponding loss in the yield of furfuryl alcohol). Hence for the conditions specified the optimum yield of furfuryl alcohol is obtained with a reaction temperature of 130° to 135° C. The yield of products recovered is not corrected for mechanical losses so that the summation of corresponding ordinates does not equal 100%.

CATALYST LIFE

The calcium-stabilized copper chromite catalyst was not deactivated in any of the experiments in this study. With one sample of catalyst 68 grams of furfural were hydrogenated for each gram of catalyst used. At the end of this series the catalyst was still active at a temperature of 140° C. Intermittent use over several weeks' time apparently had no ill effects on the activity of the catalyst. If the calcium stabilizer was left out of the catalyst a change in color occurred after intermittent use and the activity decreased.

After several hundred grams of furfural had been passed over a given sample of catalyst the surface became partially coated with an organic film not readily wet by water. Leaching with water caused a slight acidic reaction in the aqueous media. No deleterious effects on the activity of the catalyst were noted up to conversion ratios of 68 to 1. However continued use in commercial units could result in complete coating of the active surface. Presumably this could be prevented by an occasional washing of the catalyst with 2-methylfuran or other solvent to remove the polymer or decomposition product responsible for the film.

ACKNOWLEDGMENT

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Kinetic and Structural Factors Involved in Oxidation of Metals

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One of the interesting questions in the protection of metals against high temperature oxidation and corrosion reactions is whether the protection observed can be correlated with fundamental physical processes, such as ion and electron formation, and with the several structural factors of the oxide film, oxide interface, and metal. In general, the protection is associated with an oxide film of a few Ångströms to several thousand Ångströms in thickness. A study of the rate of formation and structural characteristics of such a thin film requires the use of sensitive microbalances and instruments, such as the electron diffraction camera and the electron microscope. Even with these instruments the structural factors cannot be completely determined. This paper discusses the methods used and some results of a study on several metals. The role of the secondary structure of the oxide film is presented.

THE theory and nature of the surface oxidation of metals have been a subject of increasing interest to both chemists and physicists. The usefulness of studies on the oxidation reaction to the understanding of corrosion and high temperature behavior of materials as well as to the understanding of batteries, rectifiers, and other electrochemical processes is well known. During recent years numerous attempts have been made to correlate the experimentally observed reaction rates with fundamental physical processes such as the formation and diffusion of the metal ions and electrons (*17*). These efforts have led to the application of many of the developments in solid state physics to the various physical processes involved in these reactions. However, the theory of the surface oxidation reaction is still confused. The author has felt for some time that only by a systematic attack upon the structural as well as the kinetic factors can the theory be placed on firmer ground. It is the purpose of this communication to discuss the methods and results of the author's kinetic studies together with an analysis of the structural factors studied by the electron microscope and electron diffraction techniques.

TYPE REACTIONS

Five basic reactions are fundamental to the study of the oxidation reaction.

1. $M(g) \rightleftharpoons M + g$ – degassing of the metal
2. $xM(s) + y\mathrm{O}\,(g) \rightleftharpoons M_x\mathrm{O}_y(s)$ – oxidation
3. $M_x\mathrm{O}_y(s) + y\mathrm{H}_2\,(g) \rightleftharpoons xM(s) + y\mathrm{H_2O}(g)$ – reduction with hydrogen
4. $M_x\mathrm{O}_y(s) + y\mathrm{C}\,(\text{metal}) \rightleftharpoons xM(s) + y\mathrm{CO}(g)$ – decarburization
5. $M_x\mathrm{O}_y(s) \rightleftharpoons M_x\mathrm{O}_y(g)$ – volatilization

In the above equations M refers to the metal and s and g refer to the solid and gaseous states, respectively.

The rate of formation of the oxide film, Reaction 2, is the main reaction for study. The presence or absence of gas in the metal may not only influence the reaction rate but interfere with the measurements. This gas may be removed by heating to elevated temperatures in a high vacuum according to Reaction 1. Studies on metals or alloys free from oxide films may be made if the oxide films can be reduced with hydrogen (Reaction 3), or if the oxide can be removed by the decarburization reaction, 4. The decarburization reaction makes possible the elimination of oxide films on metals or alloys which are impossible to reduce with pure, dry hydrogen. Reaction 5 provides information on the volatility of the oxide film, an important factor in the oxidation of molybdenum and tungsten.

METHODS OF STUDY

Literature. Three methods have proved useful in the study of the kinetics of thin oxide film formation. The polarimetric method has been adapted by Lustman and Mehl (*15*) for the measurement of the oxidation of copper in a continuous manner at elevated temperatures. A differential pressure method has been developed by Campbell and Thomas (*1*) and has been used for the study of a series of metals and alloys at elevated temperatures in