

presence of the other ions in the flame does not appreciably affect the photographic sensitivity for the *raies ultimes* of the alkalis, and that, in particular, a thousand-fold concentration of sodium does not interfere with the spectrophotographic detection of 10^{-5} g. of potassium, rubidium or cesium.²³

Allison states that the concentration of element 87, in the several minerals investigated, varies between 1 part in 10^{10} and 10^8 parts of the mineral.⁴ From the above deductions, it may be concluded that in order to secure spectroscopic evidence for the existence of element 87 a concentrate from 1-100 kg. of ore will be necessary, the quantity depending upon the nature of the mineral.

Summary

The ionization potential and the doublet separations of the principal series spectrum of element 87 have been evaluated by several independent methods. The values are not very concordant, but it may be assumed for purposes of further investigation that the ionization potential is approximately 4.11 ± 0.2 volts. In the spectrophotographic detection of the element, an intense line of approximate wave length 4260 ± 100 Å. is to be expected, followed by a much weaker line, of longer wave length, separated from the intense line by $550 \pm 50\mu$.

²³ These experiments were performed in the Chemistry Laboratories of the Washington Square College, New York University, during the summer of 1931.

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NON-METALLIC CATALYSTS FOR HYDROGENATION AND DEHYDROGENATION. II. THE CATALYTIC PROPERTIES OF CHROMIUM OXIDE

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In the first report on the specificity of oxide hydrogenation catalysts¹ it was pointed out that a number of difficultly reducible oxides catalyze the hydrogenation of carbon monoxide and other compounds containing the carbonyl group, but are quite inert toward activating ethylene and its homologs for hydrogenation. A continuation of this line of investigation has led to the discovery that amorphous chromium oxide constitutes an exception to the rule governing the behavior of oxide catalysts generally. In fact, the high activity of specially prepared samples of chromium oxide as catalysts for the hydrogenation of ethylene prompted a further study of the catalytic properties of this oxide and the effect of variations in the

¹ Vaughen and Lazier, *THIS JOURNAL*, **53**, 3719 (1931).

method of preparation, composition, physical condition and heat treatment.

Sabatier² lists chromium oxide as a catalyst of mediocre activity for the dehydrogenation and dehydration of alcohol, with the latter reaction predominating. Several other investigators have tested it alone and with zinc oxide as a catalyst for the synthesis of methanol.³

Hydrogenation of Ethylene and other Alkenes.—Attention was directed to the unique behavior of chromium oxide during a series of experiments in which hydrogenation occurred when a mixture of ethylene and hydrogen was passed over zinc oxide–chromium oxide catalysts of the type employed for methanol synthesis.⁴ These catalysts were prepared by the thermal decomposition of zinc ammonium chromate containing a slight excess of chromic acid. The hydrogenating activity was at first attributed to the possible presence of small amounts of some contaminating oxide capable of yielding a metal on reduction with hydrogen. The same result, however, was obtained with chromium oxide prepared by the ignition of carefully purified ammonium bichromate. Chromium oxide was also prepared by precipitation in order to eliminate the reducing action of the ignition process as a factor in the development of catalytic activity. The use of a catalyst prepared by reducing chromic acid with methanol, followed by precipitation with ammonium hydroxide, led to the fullest manifestation of catalytic activity. These and subsequent experiments have fully established the fact that capacity for catalyzing the hydrogenation of simple alkenes is an inherent property of amorphous chromium oxide.

Extensive use has been made of the hydrogenation reaction as a control method for the investigation of the influence of variables of catalyst preparation and treatment on the catalytic activity. Comparison has been made of the relative efficiency of catalysts prepared from various salts by the use of several different precipitating agents. The effect of heating the catalysts in oxidizing and reducing atmospheres has been investigated. A résumé of representative results on the hydrogenation of ethylene is presented in Table I. In every case a 20-cc. sample of catalyst was heated to 400° in a slow current of hydrogen and held at this temperature while a 7-liter sample of an equimolar hydrogen–ethylene gas mixture was passed over the catalyst in an hour.

The first five runs shown are for chromium oxides prepared by igniting ammonium bichromate. This familiar exothermic reaction, resulting in

² Sabatier–Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 252.

³ See especially Huffman and Dodge, *Ind. Eng. Chem.*, **21**, 1056 (1929); Cryder and Frolich, *ibid.*, **21**, 867 (1929).

⁴ Lazier, U. S. Patent 1,746,783, Feb. 11, 1930.

TABLE I
HYDROGENATION OF ETHYLENE OVER CHROMIUM OXIDE AT 400°

Run no.	Catalyst no.	Composition and preparation of catalyst	Comp. of H ₂	entrance C ₂ H ₄	gas, % C ₂ H ₆	Volume change, %	Ethylene conversion, %	C ₂ H ₆ in exit gas, %
1	1	Residue from ignition of (NH ₄) ₂ Cr ₂ O ₇ in deep vessel	56.9	40.7	1.9	- 0.7	2	1.6
2	2	Residue from ignition of (NH ₄) ₂ Cr ₂ O ₇ in thin layers	50.6	46.9	1.5	-37.3	80	65.0
3	3	(NH ₄) ₂ Cr ₂ O ₇ heated in vacuum to 245°	51.0	49.0	0.0	-12.3 ^a	25	16.7
4	4	(NH ₄) ₂ Cr ₂ O ₇ heated in vacuum to 500°	50.0	50.0	.0	- 1.4 ^b	3	3.7
5	3	Catalyst used in Run 3 heated in H ₂ (thermal effect)	50.0	50.0	.0	- 1.9 ^b	4	..
6	5	Chromium chromate (thermal effect during heating up)	49.5	50.5	.0	- 1.9 ^b	4	..
7	6	Cr ₂ O ₃ (by ignition of the oxalate)	50.0	50.0	.0	0.0	0	..
8	7	Cr ₂ O ₃ (by ignition of the nitrate)	50.0	50.0	.0	0.0	0	..
9	8	Chromium hydroxide (<i>ex</i> -chromate reduced in HCl soln.)	51.0	49.0	.0	-36.2	74	65.0
10	9	Chromium hydroxide (<i>ex</i> -chromate reduced in H ₂ SO ₄ soln.)	46.8	51.2	1.3	-41.0	80	77.1
11	9A	Duplicate of Catalyst 9	51.0	49.0	0.0	-43.2	88	62.4
12	10	Chrome gel (precipitated with NH ₄ OH from c. p. chloride)	52.5	47.5	.0	-36.0	76	54.0
13	11	Chrome gel (precipitated with NH ₄ OH from c. p. nitrate)	52.0	48.0	.0	-41.3	86	68.0
14	11A	Duplicate of Catalyst 11 (reduced in H ₂ overnight at 400°)	49.0	51.0	.0	-43.5	85	81.0 ^c
15	12	Chrome gel (precipitated with NaOH from chrome alum)	50.5	49.5	.0	-13.0	26	18.0
16	13	Chrome gel (precipitated with Na ₂ CO ₃ from c. p. nitrate)	50.5	49.5	.0	-15.2	31	17.0 ^d
17	14	Chrome gel (precipitated with KOH from c. p. chloride)	51.5	48.5	.0	-14.3	30	17.1
18	9	Catalyst 9 oxidized with air at 400° and reduced	48.5	51.5	.0	-40.3	79	74.5
19	2	Catalyst 2 heated in O ₂ 4 hours at 400° and reduced	50.0	50.0	.0	- 4.3 ^b	9	..
20	8	Catalyst 8 heated in O ₂ 1 hour at 500 and reduced	50.0	50.0	.0	- 2.0 ^b	4	..

^a A second run with same charge of catalyst gave almost double this contraction. ^b Contraction of gas volume only took place at beginning of run. ^c By condensation and fractional distillation exit gas contained 81.8% ethane. ^d Exit gas passed through dry-ice trap gave no liquid condensate.

the formation of a fluffy oxide having a tea-leaf appearance, has given products exhibiting erratic catalytic behavior. As indicated in the table, a variation of from 2 to 80% conversion may be obtained with successive preparations. Ignitions carried out in air, nitrogen and hydrogen have proved that the catalytic activity is not greatly influenced by the nature of the atmosphere in which the ignition is conducted. It is instead a function of the heat treatment. It has been possible to duplicate the results shown for Runs 1 and 2 by giving careful attention to the size of the mass undergoing decomposition at any one time. Ignition in deep layers permits a greater mass heat effect which results in lowered activity. A product of good activity is obtained, however, by igniting the bichromate in thin layers, which facilitates rapid dissipation of the heat. Close inspection of the ignited material reveals a non-homogeneity represented by the presence of particles of different color. It is believed that the dark colored part is the only fraction that is catalytically active. The product obtained by ignition in deep layers is much brighter green than that prepared in thin layers. It does not exhibit the glow phenomenon when heated whereas the active material glows feebly when heated to 500°.

When ammonium bichromate is heated in a vacuum at 200–250°, it slowly darkens and gradually evolves water, ammonia and nitrogen. After four or five hours there remains a glistening black residue which contains no ammonia and is slightly paramagnetic. This oxide was found to be stable at temperatures up to 400°. When further heated it suddenly glows, leaving a light green residue. Reaction tests showed that the unglowed sample was moderately active (Run 3) while samples that had been heated above the glow point were without activity (Runs 4 and 5). Ignition of chromium oxalate or nitrate at moderate temperatures yielded catalysts that were inactive for ethylene hydrogenation. This fact is especially interesting in view of the frequency with which both of these methods have been suggested and used for the preparation of active catalysts of other compositions.

The reduction of chromic acid with alcohol followed by precipitation with ammonium hydroxide is a well-known step in the separation of chromium from certain other elements. When this method was applied to the preparation of chromium oxide catalysts, the precipitates formed were different in character from those obtained under similar conditions from trivalent salts. The precipitates from reduced chromates were of a chalky blue-green color and had a powdery texture after washing and drying, whereas the hydrated oxides prepared from the trivalent salts were dark green and dried to glassy gel-like masses. Evidence will be presented later to show that the difference observed is at least partly due to a higher state of oxidation in the case of the reduced chromate catalysts. As indicated by the results of Runs 9 and 10 on the one hand and Runs 12

and 13 on the other, there is little to choose between these two sources of raw material for catalyst preparation. Both yield very active catalysts. Experience has shown, however, that the freshly precipitated gel-like products are less susceptible to the glow phenomenon. Catalysts 12, 13 and 14 prepared by use of alkalis other than ammonium hydroxide had uniformly poorer activities than those prepared with ammonium hydroxide, indicating the detrimental effect of alkali metal compounds as impurities. The reaction between ammonium chromate and a trivalent chromium salt yields a product that contains ammonia, is highly susceptible to the glow phenomenon, and consequently has a low activity for the hydrogenation of ethylene (Run 6).

Precipitation of chromium nitrate with ammonium hydroxide as represented by Catalyst 11 is perhaps the most convenient and reliable method for preparing an active chromium oxide catalyst. This catalyst was used for determining the lower temperature limits of the hydrogenation reaction. Hydrated chromium oxide becomes active at 350–370°. At higher temperatures hydrogenation is rapid, resulting in a temperature rise of about 40° in the catalyst bed. Catalyst 11 was also used for the hydrogenation of propylene and octylene. Under the conditions of Run 13, the conversion of propylene to propane was 43%. In carrying out the hydrogenation of the higher boiling compound, a hydrogen stream containing 2% of normal octylene vapor was passed over the catalyst at the usual space velocity. The iodine number of the recovered condensate indicated a conversion of 95% to saturated products. These results reveal the general applicability of the reaction.

Oxidation and Reduction Reactions of the Catalyst.—In the course of preparing samples for the hydrogenation tests it was early observed that the blue-green chromium hydroxides were reducible. A sample of Catalyst 9 dried at 400° in nitrogen evolved water copiously when the gas was changed to pure hydrogen. This reduction was accompanied by a change in color from the original blue-green to a greenish brown. Careful treatment with air led to a black product which could be reduced again. The reduced oxide was pyrophoric and very active for hydrogenation. On the other hand, if the oxidation was carried out with oxygen at 500°, subsequent reduction yielded a bright green product that was catalytically inactive and apparently no longer susceptible to further oxidation or reduction. The hydrated chromium oxide gels prepared from chromic salts appeared to be unaltered by heating in air or hydrogen.

In order to obtain more accurate data on the reduction reactions observed, the hydrogen consumption of weighed analyzed samples was determined in apparatus designed especially for the study of oxide reductions.⁵ At 400° Catalyst 9 (*ex-sulfate*) consumed about 0.75 mole of hydrogen

⁵ Taylor and Starkweather, *THIS JOURNAL*, **52**, 2314 (1930).

per gram atom of chromium whereas only 0.5 mole is theoretically required to reduce CrO_2 to Cr_2O_3 . However, the catalyst contained sulfate equivalent to 3.8 weight per cent. of sulfur. That this sulfate was reduced at least in part to sulfide was evidenced by the formation of hydrogen sulfide during the reduction. The hydrogen consumption was in excess of that necessary for complete reduction of the sulfate, which shows that this was not the only reduction taking place. Catalysts 10 and 11 prepared as the hydroxides from chromium chloride and nitrate, respectively, required for reduction only 0.2 mole of hydrogen per gram atom of chromium. The reduction data cannot be interpreted accurately on account of the fact that it was practically impossible to wash the chromium hydroxide samples completely free from salts. In an attempt to determine the initial state of oxidation, several of these samples were evacuated at high temperatures with a Toepler pump and in every case the evolved gases contained, in addition to oxygen, acidic components corresponding to the salts used in preparing the catalysts. The reduction data are sufficiently accurate however to establish the wide difference in oxidation level of the products from the alcohol-reduced compounds and those from commercial trivalent salts.

x-Ray Analysis.—Dr. A. W. Kenney of this Laboratory has obtained Debye-Scherrer diffraction patterns of several catalysts tested for ethylene hydrogenation. Exposures were made on catalysts before and after use and in the glowed and unglowed condition. Catalysts 1, 6 and 7, all of which were prepared by ignition processes and were catalytically inactive, gave the characteristic pattern of a well-defined crystalline chromium sesquioxide.⁶ Catalyst 2, which was prepared by a more gentle heat treatment and was found to be active, yielded a diagram indicating dilution of the crystalline oxide with amorphous material. None of the precipitated catalysts, whether prepared from reduced chromic acid or from chromic salts, yielded diffraction patterns when exposed to x-rays, demonstrating the amorphous character of these materials. Catalyst 9 was unchanged in this respect after having been employed for hydrogenation, but Catalyst 11 contained a trace of crystalline oxide after only one hour of use. Glowing of any of the amorphous catalysts resulted in the formation of products having the typical diffraction pattern of chromium sesquioxide. Oxidations and reductions carried out under conditions leading to the formation of the light green reduction product were also found to develop the crystalline state.

Dehydrogenation and Dehydration of Ethanol.—The effect of the glow phenomenon on the catalytic characteristics of chromium oxide is further illustrated by results obtained in a series of experiments on the catalytic decomposition of alcohol. Ethanol vapor was passed over small samples of Catalysts 11 and 11A under the conditions indicated in Table II. Run 2 was made with a sample that had been heated in air to 600° before

⁶ Davey, *Phys. Rev.*, [2] 21, 716 (1923).

use while Runs 3-5 were made consecutively on a sample of a duplicate catalyst. During the interval between Runs 4 and 5, the catalyst was heated in hydrogen to 530°, at which temperature it glowed with an observed rise in temperature of about 100°. The data presented in the table represent the performances of the respective catalysts during the first hour of use.

TABLE II
DECOMPOSITION OF ETHANOL

Run	Catalyst	Catalyst vol., cc.	Alcohol flow, cc./hr.	Temp., °C.	Gas evolution, liters/hr.	H ₂	Gas composition, % C ₂ H ₄	% C ₂ H ₆
1	No. 11	3	60	375	2.62	42.8	48.6	3.1
2	No. 11 (heated to 600°)	3	62	375	1.51	57.5	35.4	..
3	No. 11A	5	60	415	5.40	40.4	50.6	3.9
4	No. 11A	5	60	430	6.20	42.6	47.7	4.5
5	No. 11A (glowed)	5	55	430	3.38	66.4	1	1.8
6	ZnO	3	90	380	6.20	69.3	25.8	0.0

Although the activity of the catalyst is impaired by glowing, it is not destroyed to as great an extent for dehydrogenation as for the hydrogenation of ethylene. This fact is also evident in the last column of the table. The difference in total dehydrogenation and dehydration activity for Runs 4 and 5 as measured by gas evolution is only about 45%, whereas the decrease in saturated hydrocarbon formation is about 78%. Catalyst 11 had an activity for alcohol decomposition equal to 42% of that of zinc oxide (*ex-oxalate*) at 375°, whereas Sabatier's⁷ chromium oxide was 70% as active as his zinc oxide. Sabatier also reported a dehydration-dehydrogenation ratio of 10 compared with 1.1 obtained in this work. Both researches⁸ are in accord, however, in finding that heat treating the catalyst shifts the ratio in the direction of a greater proportion of dehydrogenation. As in the case of zinc oxide,⁹ a shift in the temperature of decomposition of alcohol over chromium oxide has little effect on the ratio of dehydration to dehydrogenation.

Dehydrogenation of Cyclohexane.—The fact that amorphous chromium oxide is capable of catalyzing the hydrogenation of ethylene suggested a test of its activity in the dehydrogenation of hydrocarbons. Cyclohexane was chosen for the experiment because the position of the equilibrium in the temperature range required is favorable while that of the dehydrogenation of ethane is unfavorable. Cyclohexane was passed over 3-cc. samples of Catalyst 11 at the rates of flow indicated in Table III. Glowing was induced in the catalyst used for Run 4 by heating the unglowed oxide to 510°. Several other oxides were employed as controls.

⁷ Sabatier-Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 252.

⁸ Sabatier and Mailhe, *Ann. chim. phys.*, [8] 20, 304 (1910).

⁹ Adkins and Lazier, *THIS JOURNAL*, 48, 1671 (1926).

TABLE III
 DEHYDROGENATION OF CYCLOHEXANE

Run	Catalyst	C ₆ H ₁₂ flow, cc./hr.	Temp., °C.	Gas evolution, liter/hr.	Benzene in condensate, %
1	Glass wool	60	420-500	0.00	0.08
2	No. 11	57	410	1.50	1.56
3	No. 11	78	430	2.24	3.12
4	No. 11 (glowed)	110	410	0.00	..
5	ZnO	80	410-480	.16	0.33
6	SiO ₂ gel	80	410	.00	.0
7	Al ₂ O ₃	80	410	.00	.0

While cyclohexane is apparently stable at temperatures up to 500° in the absence of an active surface, as shown by the results obtained with glass wool, the compound is dehydrogenated by unglowed chromium oxide. Zinc oxide and glowed chromium oxide, on the other hand, are relatively inactive as catalysts for the reaction even at much higher temperatures. Alumina and silica gel are also non-catalysts for the reaction in the temperature range studied.

Other Reactions Catalyzed by Chromium Oxide.—Several chromium oxide catalysts have been tested for the high pressure synthesis of methanol in the course of a comprehensive survey of the subject. The results given in Table IV were obtained with gaseous mixtures containing about 58% hydrogen, 35% carbon monoxide and 1 to 2% each of nitrogen, carbon dioxide and methane. The yields are reported on the basis of a 100-cc. catalyst sample, although a lesser quantity was used in some of the experiments.

 TABLE IV
 METHANOL SYNTHESIS WITH CHROMIUM OXIDE CATALYSTS

Run	Cat. no.	Catalyst composition	Temp., °C.	Pres., atm.	Space velocity	Yield of crude condensate ^a	Composition of condensate		Yield pure methanol ^a	Yield higher alcs. ^a
							% MeOH	% Higher alcs.		
1	12	Hydrated Cr ₂ O ₃ Gel	439	290	5,000	27.5	40	..	11.0	...
			440	290	10,000	36.0	60	..	22.5	...
			450	290	20,000	74.0	70	..	52.0	...
2	6	Cr ₂ O ₃ (<i>ex</i> -oxalate)	375	280	10,000	43.0	41	..	17.6	...
			420	280	10,000	36.0	40	..	14.5	...
			450	280	10,000	39.0	34	23	13.2	9.0
3	1	Cr ₂ O ₃ (<i>ex</i> -(NH ₄) ₂ CrO ₄)	425	280	10,000	14.0	48	7	6.7	1.0
			450	280	10,000	19.0	30	17	5.7	3.2
4	5	Chromium chromate	400	272	19,200	22.0	63	14	13.9	3.1
			448	272	19,000	26.0	49	22	12.7	5.7

^a Yields are expressed as cc. per 100 cc. of catalyst per hour.

In general the activity of chromium oxide catalysts for this reaction is low as compared with certain other single oxides. Zinc oxide, for example, when prepared by igniting the oxalate,¹⁰ gives a yield of 70 cc. of pure methanol per 100 cc. of catalyst per hour when used under the first set of

¹⁰ Lazier, U. S. Patent 1,746,781, Feb. 11, 1930.

conditions of Run 2. Chromium oxide gel is the most efficient chromium oxide catalyst. When removed from the reaction vessel, this catalyst was unchanged in appearance, whereas Catalysts 1, 5 and 6 had assumed the bright green color characteristic of a glowed chromium oxide. Although none of the samples was heated above the temperatures indicated, the poorer showing made by each of the last-named samples is in all probability due to the type of sintering which results in crystallization and in the case of ethylene hydrogenation causes a much larger decrease in catalytic activity.

Like many other oxides, chromium oxide, particularly in the hydrated form, is an active catalyst for the conversion of water gas and steam to hydrogen and carbon dioxide. The reaction takes place at temperatures up to 500° without carbon deposition. The work of Beekley¹¹ indicates that preservation of the activity of the catalyst is contingent upon prevention of the glow phenomenon, although no indication is given as to whether the sensitivity in this case corresponds with that observed for hydrocarbon hydrogenation or for alcohol synthesis and decomposition.

Observations on the Glow Phenomenon.—The large number of tests incident to the investigation of the catalytic properties of chromium oxide have furnished an excellent opportunity for observing the glow phenomenon as it affects this particular oxide. It has been found that the transformation is not associated with any one source of the oxide or method of preparation but with all amorphous catalysts. The phenomenon is not dependent on a gel structure as ordinarily manifested by the outward appearance of a precipitate, since the powdery chromium oxides obtained from reduced chromates glow even more readily than those of a gel-like character. Amorphous chromium oxide glows when strongly heated regardless of the nature of the atmosphere which happens to surround it. If the nature of the gas affects the temperature of glowing, as is sometimes the case, it is because a reaction such as reduction of a higher oxide or oxidation of adsorbed hydrogen is initiated on the surface which produces heat effects that accelerate what would otherwise be a spontaneous transformation. No specific state of oxidation appears to be necessary since glowing has been experienced with both oxidized and reduced samples. The glow may take place without evolution or adsorption of gases but water is copiously evolved. In case the unglowed oxide is in a higher state of oxidation than Cr_2O_3 , oxygen is eliminated in the process, leaving a residue of Cr_2O_3 .

Discussion

The outstanding fact uncovered by the experimental work is that chromium oxide is inherently capable of bringing about the hydrogenation of the alkene bond, a distinction which sets it apart from all of the other hydrogenating-dehydrogenating oxides so far studied. On account of the several

¹¹ Beekley, U. S. Patent 1,789,538, Jan. 20, 1931.

methods used for the production of active catalysts and the precautions taken in the purification of the starting materials, it is not reasonable to attribute the results obtained to the presence of an impurity. Assuming that in order to obtain hydrogenation, activation of both hydrogen and the compound to be hydrogenated is necessary, it is apparent that chromium oxide differs from the other oxides in that it is *capable of activating hydrocarbons*, for many oxides are capable of catalyzing the hydrogenation of carbonyl groups in processes which must also require hydrogen activation. A practical application of this concept is found in the reported use of chromium oxide as a major component of catalysts for the destructive hydrogenation of coal and petroleum,¹² and it is possible that such a catalyst might also be useful for other reactions of the unsaturated hydrocarbons.

Equilibrium considerations and the necessity of avoiding the glow phenomenon have precluded an attempt to investigate the reverse reaction of dehydrogenation of simple saturated hydrocarbons. It can be assumed, however, that the cyclic hydrocarbons should behave in a manner analogous to the alicyclic series; in fact, the same differences between zinc and chromium oxides observed in ethylene hydrogenation were found to hold for the dehydrogenation of cyclohexane. The same forces are apparently at play in these two cases. This is another instance in support of the proposal that the mechanism of hydrogenation and dehydrogenation is the same.

Another important point established by the experimental work is the discovery that the capacity of chromium oxide for hydrogenation and dehydrogenation of hydrocarbons is linked to the amorphous form alone. x-Ray data are readily applicable to the detection of crystalline material, but they cannot be applied with equal facility to the detection of amorphous compounds when crystalline material is also present. In spite of this limitation of the experimental method, it has been shown that any treatment leading to glowing and the consequent development of crystalline material in the oxide resulted in a serious and usually total loss of activity toward hydrocarbons. The same factors however caused relatively minor effects on the activity toward oxygenated compounds as illustrated by the results on methanol synthesis and dehydrogenation of ethanol. The amorphous state is not in general a prerequisite for catalytic activity since the hydrogenating oxides previously studied were all crystalline in character.

The high-temperature loss of capacity for hydrocarbon activation appears to contribute to a further understanding of the mechanism of the glow phenomenon. Weiser¹³ believes that "there is little doubt but that the glow is due to a very sudden decrease in the large surface of the oxides

¹² See especially British Patent 251,264 filed April 14, 1926, and 311,251 filed December 5, 1927.

¹³ Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., New York, 1926, p. 79.

prepared by precipitation" while Böhm¹⁴ and Blanc¹⁵ have reached the conclusion as a result of x-ray studies and thermal analyses that the transformation is only a change from the amorphous to crystalline state. Measurement of catalytic activity should provide a sensitive test for any substantial decrease in surface. The effect of the glow phenomenon on activity toward hydrocarbon activation, if taken alone, would be exactly what to expect if Weiser's explanation is the correct one. Our x-ray findings confirm those of Böhm, and the results on alcohol decomposition and methanol synthesis indicate no greater loss of active surface than may be readily obtained by mildly sintering a crystalline oxide catalyst. While it is believed that the catalytic observations reported have a significant bearing on the mechanism of the glow phenomenon, it is inadvisable in the present state of our knowledge to attempt a more elaborate interpretation of the results obtained.

The preparation of an oxide capable of glowing by partial ignition of ammonium bichromate throws some light on the mechanism of the decomposition of this salt. It is of interest to note that the heat evolved is due only in part to the oxidation of ammonia. The remainder is furnished by the glow phenomenon. It is evident that the arrangement of oxygen and chromium atoms in ammonium chromates is as unstable as in the precipitated trivalent oxides. Mellor¹⁶ states that chromium oxide prepared by igniting ammonium bichromate is amorphous. In view of our experimental results, this statement holds good only for the oxide prepared at low temperatures in a vacuum.

The theoretical treatment of contact reactions is usually based on the concept of a crystalline catalyst in which the surface presents a definite pattern which is held responsible for the direction of the reaction. In an extension of these ideas the authors¹⁷ explained the non-activity of oxides for hydrogenation of alkenes by assuming that the residual valences of the metal atoms of the surface which ordinarily function as hydrogenation centers were dissipated in metallic oxides by the surrounding oxygen atoms. The present case of amorphous chromium oxide cannot be treated in the same way, since as far as we know there is no regular arrangement of atoms in the surface of amorphous materials.

The dehydrogenation of cyclohexane over *amorphous* chromium oxide constitutes a formidable obstacle to Balandin's theory¹⁸ requiring a surface lattice of a certain configuration. The theory further requires that before catalysis can occur the permissible spacing of the atoms must be within

¹⁴ Böhm, *Z. anorg. allgem. chem.*, **149**, 217 (1925).

¹⁵ Louis Blanc, *Ann. chim.*, [10] **6**, 182 (1926).

¹⁶ Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, 1931, Vol. XI, p. 177.

¹⁷ Vaughen and Lazier, *THIS JOURNAL*, **53**, 3719 (1931).

¹⁸ Balandin, *Z. physik. Chem.*, **B2**, 289 (1929).

narrow limits the symmetry of the active points of the catalyst coinciding with the symmetry of the adsorbate. Unlike the hydrated chromium oxide catalyst, zinc oxide is crystalline, and the arrangement of the zinc atoms is similar to that of metallic zinc, but the spacings between zinc atoms in the oxide are wider than in the case of the metal. In zinc oxide the interatomic distance is about 3.25 Å. as compared with 2.8 set by Balandin as the upper limit for an active hydrogenation catalyst.

A discussion of the relationship of the physical, chemical and catalytic properties of chromium oxide should not be concluded without reference to the possible role played by water. Most of the active preparations studied were highly hydrated, the water being so tightly held that it was not removed in appreciable quantities at the relatively high temperatures of the catalytic tests. The catalyst prepared by the controlled ignition of ammonium bichromate was no exception, since this oxide was found to retain a portion of the water formed by the oxidation of ammonia during ignition. On the other hand, the glow phenomenon results in an effective and probably non-reversible expulsion of water which must of itself alter the chemical nature of the surface. The changes in catalytic properties of chromium oxide resulting from the glow phenomenon cannot be definitely associated either with the chemical changes caused by dehydration or the physical changes manifested by x-ray analysis.

Experimental Part

Catalyst Preparation.—On account of the large number of catalysts prepared and tested it will be impossible to give the complete details of preparation of each. In presenting this section care has been taken to set forth only such information as, in the present state of our information, is regarded necessary to obtain reproducible results. Catalysts 1 and 2 were prepared by igniting *c. p.* ammonium bichromate. The salt was freed from traces of iron by dissolving in strong ammonia solution, allowing to stand at 40–50° and removing the iron hydroxide sludge by filtration. For Catalyst 1, 100 g. of the dry salt was placed in a 650-cc. loosely covered casserole and heated in a muffle furnace at 400° for thirty minutes, no effort being made to control the rate of decomposition or temperature of the mass. In preparing Catalyst 2, 1-g. portions of the salt were warmed over a flame until ignition was initiated. Catalysts 3 and 4 were prepared by slowly heating 15-g. samples of ammonium bichromate in an oil-bath under the vacuum produced by a Cenco Hyvac pump. In the first case decomposition was observed to set in at about 200° and the sample was not heated above 245°. For the second preparation, the temperature was raised to 500° after four hours of heating at the lower temperature. A second change in the character of the product was evident at about 485°. In the preparation of Catalysts 5 and 6 chromium nitrate and oxalate, respectively, were heated for four hours in a muffle furnace controlled at 400°. The following procedure was employed for the preparation of Catalysts 8 and 9. A hot solution containing 150 g. of ammonium bichromate dissolved in 500 cc. of water was poured slowly into a boiling solution of 200 cc. of sulfuric acid (or such a volume of concentrated hydrochloric acid as is equivalent to the sulfuric acid indicated) and 150 cc. of methanol in 500 cc. of water. The reduction product was diluted with 5 volumes of water, cooled to room temperature and precipitated by the addition of a slight excess of ammonium hydroxide.

Catalysts 10-14 inclusive were prepared by the addition at room temperature of the appropriate alkali precipitating agents to 0.04 molar solutions of C. P. trivalent chromium salts. All precipitated catalysts were washed five to ten times by decantation with a volume of water at least equal to the mother liquor. In one case a dialyzed sample was found to give the same catalytic results as an undialyzed sample. Catalyst 5 was prepared by adding an equivalent of ammonium chromate to chromium nitrate, the other conditions being the same as for the precipitated hydroxides. All of the precipitated catalysts were dried at 110°, and suitable physical form was obtained by breaking up the filter cake and collecting the 8-14 mesh material. These products were subject to a 20% shrinkage when heated in place in the reaction apparatus but no allowance was made for this in measuring the catalyst charges. Catalysts prepared by ignition processes were granulated by briquetting. The samples of zinc oxide and alumina used for reference catalysts were prepared by ignition of zinc oxalate and aluminum hydroxide, respectively.

Apparatus and Experimental Method.—The apparatus used for the hydrogenation of alkenes was the same as that described for this purpose in the earlier paper.¹⁹ In every case the catalyst sample was heated to the reaction temperature in a slow stream of hydrogen. All oxidations or reductions on samples to be tested for this reaction were made in place by by-passing the gasometers. The furnace temperature was controlled by a Republic pyrometer while the temperature of the interior of the catalyst bed was simultaneously recorded by a Leeds and Northrup controller-recorder.

Gas analyses were made on a Fisher Universal Gas-Analyzing Apparatus. The necessity of burning only a small aliquot of samples containing a high ethane content often led to somewhat discordant results, necessitating repeated analyses. In view of Lenher's discovery²⁰ that a trace of oxygen is able to initiate a polymerization of ethylene to higher alkenes, it was desirable to determine whether any saturated hydrocarbon other than ethane was formed. In two representative experiments on the hydrogenation of ethylene, analyses of the effluent gases were made by Dr. D. F. Babcock in the Podbielniak fractional-distillation apparatus.²¹ These data were in very good agreement with those obtained by the combustion method and proved conclusively the absence of saturated hydrocarbons other than ethane. In the preparation of Table I, the ethylene conversions were calculated from the inlet gas compositions and contractions observed on passage over the catalysts. The analyses for ethane served to confirm the conclusions reached in this way. In some cases, particularly in connection with the dehydrogenation experiments, the gas analyses reported do not equal 100% for the reason that negligible amounts of nitrogen, carbon dioxide or carbon monoxide initially present in the apparatus or formed as side reactions are not included in the tabulated data.

The experiments reported on the dehydrogenation of ethanol and cyclohexane were carried out in apparatus patterned after that of Adkins and Nissen.²² The accuracy, efficiency and convenience of this apparatus have been improved by so many alterations and additions over a period of six years' use in this Laboratory that it is thought worth while to describe the improved set-up in some detail. The added features are (1) automatic regulation of the mercury head of the feed device, (2) provision for refilling without disassembling, (3) semi-automatic control of the gasometer pressure and volume and (4) provision for gas sampling at constant pressure and without interrupting the progress of the experiment. By mounting the reaction tube and furnace in a vertical position, channeling of the catalyst bed due to shrinkage is prevented. With a 46-cm. reaction

¹⁹ Vaughen and Lazier, *THIS JOURNAL*, **53**, 3719 (1931).

²⁰ Lenher, *ibid.*, **53**, 3752 (1931).

²¹ Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931).

²² Adkins and Nissen, *THIS JOURNAL*, **46**, 140 (1924).

furnace a separate preheating furnace may be omitted, the indentations in the upper part of the reaction tube furnishing an adequate heating surface.

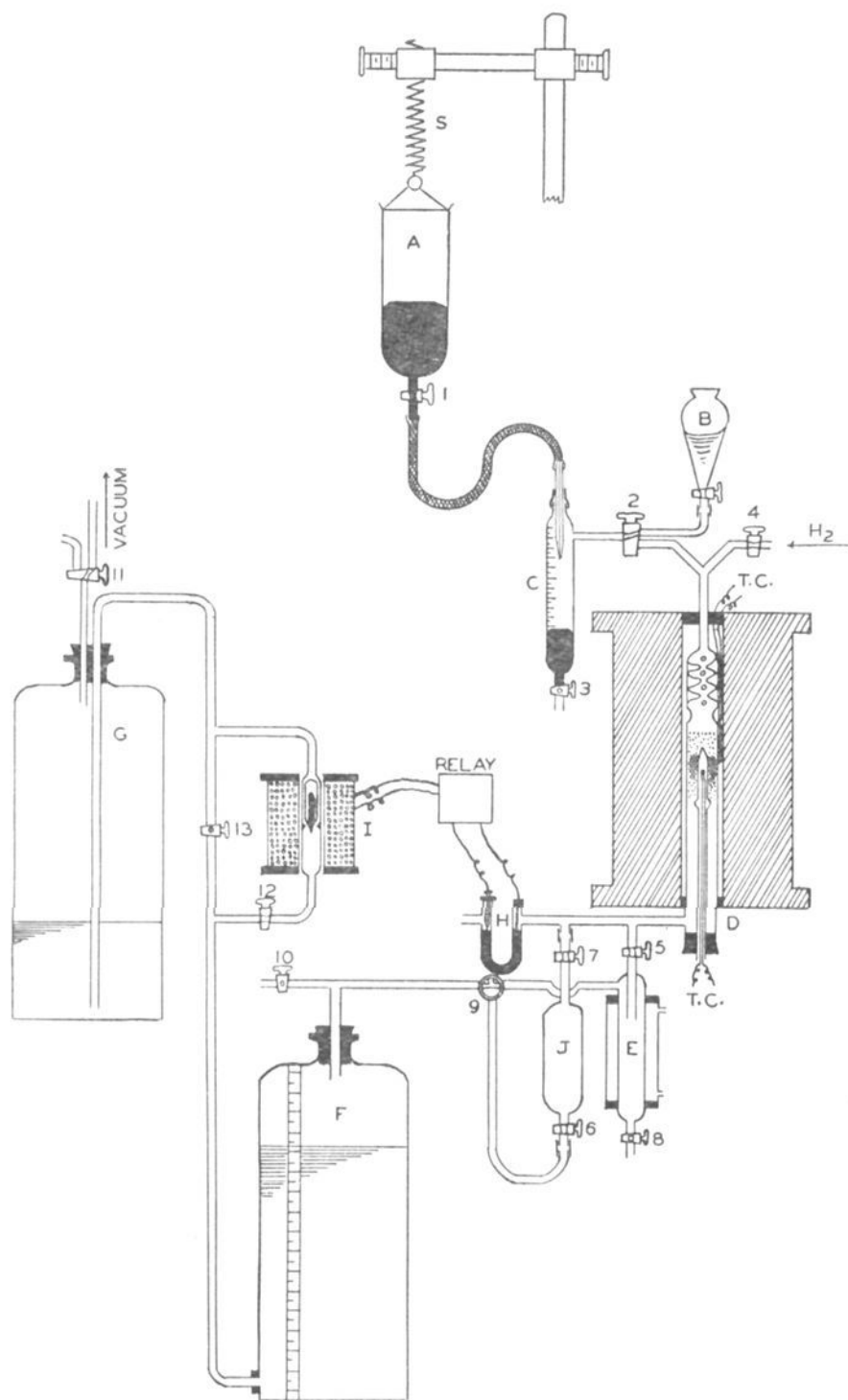


Fig. 1.—Dehydrogenation apparatus.

The liquid to be treated is stored in the flask B, from which it is drawn to fill the buret C. From here it is displaced into the reaction tube D with mercury, which enters the buret at a constant rate through a capillary. Refilling is accomplished by turning Stopcock 2 and draining out the mercury at 3. The characteristics of the springs and the diameter of the mercury reservoir A are so chosen as to maintain a constant head of mercury on the capillary.

A Y-tube is provided at the head of the reaction vessel to permit the passage of hydrogen over the catalyst during its pretreatment. The catalyst is held in place in the reaction tube with plugs of glass wool, the lower plug being supported by a button on the thermocouple well, through which a thermocouple reaches the interior of the catalyst bed. Another thermocouple is placed at the catalyst level against the outside of the tube. Temperature control and records are obtained as outlined for the ethylene hydrogenation apparatus.

The liquid products are condensed in the water-cooled trap E, and the gaseous products pass into the gasometer F. Water is drawn out of the gasometer by suction on bottle G, and the rate of withdrawal is controlled by the manometer H and solenoid valve I. The collecting system used in this work was capable of receiving a gas evolution of about 20–25 liters per hour, with a deviation from atmospheric pressure of only a few millimeters. At definite intervals the exit gas was sampled by turning stopcock 9, which permitted gas to displace the water in sample bottle J into the gasometer F. Saturated salt solution was used as the retaining liquid, and a little of it was left in the sample bottle when sampling in order to displace dissolved gases from the condensed alcohol. Small quantities of benzene in cyclohexane were determined by use of the refractometer.

The apparatus assembly used for methanol synthesis was essentially the same as that described by Lewis and Frolich.²³ The average duration of operation at each set of conditions was four hours, the same charge of catalyst being used at a number of different temperatures.

Materials.—Ethylene and hydrogen of 98–99% purity were procured from commercial storage cylinders. Propylene was prepared by the catalytic dehydration of isopropanol over an alumina catalyst. Absolute ethanol was used for the dehydrogenation tests. The cyclohexane and octylene were Eastman Nos. 702 and 1821. The synthetic water gas used for methanol synthesis was prepared by mixing cylinder hydrogen with carbon monoxide prepared by blowing carbon dioxide over heated coke.

In addition to references already made, the authors also acknowledge the assistance and helpful criticism of Drs. G. B. Taylor and H. G. Tanner of the Experimental Station staff.

Summary

Amorphous chromium oxide has been found to be an active catalyst for the hydrogenation of ethylene, propylene and octylene and for the dehydrogenation of cyclohexane, differing in this respect from any other hydrogenating oxide tested. Experiments on a variety of catalyst preparations bear out the conclusion that this behavior is not associated with any particular impurity, source of materials or method of preparation but is inherently associated with the amorphous state of chromium oxide. Any treatment leading to glowing with consequent development of crystalline material in the oxide greatly impairs or destroys activity for the hydrocarbon reactions. Activity for methanol synthesis or dehydrogenation of ethanol is less affected by such treatment.

Chromium oxide is quite active for alcohol decomposition, giving about 50% each of dehydration and dehydrogenation. Heat treatment causes a shift in the ratio in the direction of a greater proportion of dehydrogenation.

²³ Lewis and Frolich, *Ind. Eng. Chem.*, **20**, 285 (1928).

A number of observations on the glow phenomenon have been recorded, the most interesting and important fact uncovered being that the glow phenomenon, which invariably results in the crystallization of the chromium oxide, also results in the loss of capacity of the catalyst for activating hydrocarbons. The bearing of these experimental results on current theories of catalysis is discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE THEORY OF THE GLASS ELECTRODE. II. THE GLASS AS A WATER ELECTRODE

BY MALCOLM DOLE

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Introduction

The inability of the glass electrode to function as a perfect hydrogen electrode in alkaline solutions has recently been explained¹ on the assumption that sodium or other positive ions as well as hydrogen ions may have an appreciable mobility across the aqueous solution glass boundary. This theory, however, fails to account for the interesting errors of the glass electrode in very acid solutions recently discovered by MacInnes and Belcher and by Buchböck² inasmuch as the current carried by the sodium ion across the boundary becomes less and less as the hydrogen-ion concentration increases and the hydrogen ion carries more and more current. Since

¹ Dole, *THIS JOURNAL*, **53**, 4260 (1931). The author wishes to publish the following corrections to this paper. On page 4271 a statement was made concerning the work of Lengyel which is, perhaps, a bit misleading in that Lengyel's experimental procedure was not fully described. Lengyel considered his quartz membranes as condensers, but since he used his electrometer as a null point instrument, the relative capacity of the quartz membrane and of the condenser did not matter; it is only on attempting to measure the potential difference directly by the electrometer deflections that the capacity of the electrometer must be considered in relation to the capacity of the quartz membrane.

The author also wishes to emphasize further concerning his theory of the glass electrode that the experimental equation is highly empirical in that the slope and intercept have to be found from the data; they cannot be calculated. The theoretical significance of the equation rests in the analogy between the empirical equation and one derived on the basis of liquid junction theory (after making several hypothetical assumptions). Hence in reading the author's second paper on the theory of the glass electrode this should be borne in mind.

A misunderstanding has arisen over the mention of the name of Dr. MacInnes in reference 1 of the author's first paper. Dr. MacInnes does not subscribe to the author's theory as given in this paper; Dr. MacInnes' own theory of the glass electrode appeared in a paper previously published with Belcher, *THIS JOURNAL*, **53**, 3315 (1931).

² Buchböck, *Z. physik. Chem.*, [A] **156**, 232-236 (1931); MacInnes and Belcher, *THIS JOURNAL*, **53**, 3315 (1931).