selective manner and, therefore, that the linear relation in 2 need give no true concept of the catalyst surface.

4. An indirect method of poisoning active copper with oxygen appears to be selective in character.

5. Direct poisoning of active copper with nitrous oxide also appears to be selective.

6. All of the experimental evidence is considered to indicate (a) that the copper surface is non-uniform and (b) that at 0° the hydrogenation of ethylene proceeds almost exclusively on a relatively few surface types, probably of intermediate character.

7. The interpretation of the experimental evidence is consistent with an exponential distribution of centers active at 0° in catalyzing the ethylene–hydrogen reaction.

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[Contribution from the Chemical Laboratory of the University of Nebraska]

A Study of the Dehydration of Hydrated Cobaltic Oxide

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The literature[1,2,3,4] gives various temperatures, ranging from about 150 to 385°, at which hydrated cobaltic oxide begins to decompose into Co_3O_4, oxygen and water. The observations made in this Laboratory indicate the reason for the apparent disagreement of the investigators.

Experimental

Various lots of hydrated cobaltic oxide were prepared by alkaline decomposition of chloropentammino-cobalti chloride, as recommended by Hüttig and Kassler[1] except that the colloidal oxide was isolated by centrifuging instead of using a membrane filter. The oxide was then dried two days over concentrated sulfuric acid in a vacuum desiccator and ground in an agate mortar. Analyses of the partially dehydrated oxides showed the practical absence of divalent cobalt, and a water content corresponding to about $Co_2O_3 \cdot 1.6H_2O$, or a calculated value of about 15% water and 85% of the hypothetical anhydrous Co_2O_3. The oxide thus prepared was then dehydrated at various temperatures. This was done by passing highly purified air over the oxide samples while the latter were constantly agitated with a mechanical shaker to provide uniform conditions. The approximate progress of the dehydration was determined at twelve or twenty-four-hour intervals by weighing the amount of water collected in dehydrite absorption tubes connected to the air exhaust. Each run was continued until the loss of water decreased to about 0.5 mg. in twenty-four hours. This usually required from two to four days. The oxide was then analyzed for trivalent cobalt by the oxalate–permanganate method as recommended by LeBlanc and Möbius[5] and for water by heating the oxide to red heat in a combustion furnace, using a dehydrite absorption tube to collect the water.

Table I

Results of Experiments

Temp., °C., ±3°	% Co_2O_3[a] remaining	% H_2O remaining	% H_2O, calcd. for $Co_2O_3 \cdot 1H_2O$
155	35.3	4.6	3.83
168	19.0	3.8	2.06
177	17.3	2.7	1.88
195	13.3	3.1	1.44
205	19.3	2.3	2.09
220	9.7	1.5	1.05
235	10.3	1.4	1.12
260	15.7	2.2	1.70

[a] Hypothetical anhydrous oxide.

It was noticed in all cases that the rate of dehydration is very slow up to 90°, but in the range from 100 to 180° rapid dehydration takes place. For example, a 1.5-g. sample heated for twenty-four hours at 105° lost 0.006 g.; during the next forty-eight hours at 180° it lost an additional 0.163 g.; then during the next eighty-four hours at 250°, only 0.003 g. additional. In some cases, however, the dehydration at the end of 200° treatment was not nearly as complete as shown above for 180°, and a considerable amount of water continued to be evolved at still higher temperatures.

Further information was obtained in attempts to prepare anhydrous Co_2O_3 by oxidation with

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(1) G. Hüttig and R. Kassler, *Z. anorg. Chem.*, **184**, 283 (1929).

(2) G. Natta and M. Strada, *Gazz. chim. ital.*, **58**, 428 (1928).

(3) F. Merck and E. Wedekind, *Z. anorg. allgem. Chem.*, **186**, 68 (1930).

(4) T. Carnelley and J. Walker, *J. Chem. Soc.*, **53**, 90 (1888).

(5) M. LeBlanc and E. Möbius, *Z. physik. Chem.*, **142**, 170 (1929).

dry oxygen at relatively high pressures. Large samples of dry Co_3O_4, prepared by igniting cobaltous carbonate in air, were placed in an electrically heated high pressure bomb. These were subjected to about 100 atm. of oxygen pressure at various temperatures ranging from 200 to 400°, followed by rapid cooling to room temperature at full pressure. The results were negative throughout. Further experiments were then carried out as follows. A large porcelain boat containing about 5 g. of very pure, partially hydrated, cobaltous carbonate was placed in the hot end of the bomb, and another boat containing freshly ignited calcium oxide was placed in the cooler end to absorb carbon dioxide and water. One experiment (A) of this type was carried out at 330° for sixty-eight hours at 107 atm.; another (B) at 275° for forty-four hours at 72 atm. A different type of experiment (C) was then tried in which partially dehydrated cobaltic oxide was heated for twenty hours with calcium oxide as dehydrating agent at 315° and 127 atm.; followed by twenty hours with phosphorus pentoxide as dehydrating agent at the same temperature and pressure. The following results were found:

TABLE II

	% Co_2O_3* remaining	% H_2O remaining	% H_2O calcd. for $Co_2O_3 \cdot H_2O$	% CO_2
(A)	9.5	1.15	1.03	0.5
(B)	15.3	2.03	1.66	.6
(C)	7.9	1.05	0.86	

Conclusions

Table I shows that decomposition takes place slowly in the 150° temperature region as claimed by Hüttig and Kassler.[1] Both Tables I and II furnish evidence in support of their observations that cobaltic oxide is stable only with a minimum water content corresponding to the monohydrate. The irregularities in "% Co_2O_3 remaining" at increasing temperatures (Table I) are believed to be due to the differences of speed with which water vapor could be physically removed from the various samples having different physical properties. Since no attempt was made to centrifuge the various hydrated oxide preparations the same length of time, their porosity and particle size, no doubt, varied enormously. It should be noted that Hüttig and Kassler in their study of the water vapor equilibrium pressures also found decided variations with different samples.

Since the hydrated oxide sample used in (C) contained about 85% hypothetical Co_2O_3 and about 15% water before dehydration at 315°, it appears that the oxygen dissociation pressure of anhydrous Co_2O_3, formed by the dehydration, is greater than 127 atm. at 315°. Experiments (A) and (B) show, however, that the reaction is reversible in presence of water, and that the amount of divalent cobalt which can be oxidized to cobaltic oxide is, in general, proportional to the amount of water still available to form the monohydrate.

The observations throughout seem to indicate that the prolonged existence of rather large amounts of residual hydrated cobaltic oxide, at temperatures much higher than the 150° region, can be explained on the basis of a retarded rate of dehydration in the inner regions of the oxide particles, due to a very slow rate of outward diffusion of the liberated water. It would therefore seem plausible that wet hydrated cobaltic oxide might be dried for short periods of time, at the higher temperatures mentioned by some investigators, without appreciable decomposition into Co_3O_4, provided the physical conditions are unfavorable for the rapid and complete escape of the liberated water.

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