[CONTRIBUTION FROM THE ROHM AND HAAS CO.]

An X-Ray Diffraction Study of the Copper Chromites and of the "Copper-Chromium Oxide" Catalyst[1]

BY JAMES D. STROUPE

The "copper–chromium oxide" hydrogenation catalyst, effective for the liquid phase hydrogenation of some types of organic compounds,[2,3] is normally prepared by decomposing a copper ammonium chromate at low temperatures to give a material reported as "copper–chromium oxide," "copper chromite," "copper oxide–chromite," etc.[2] Of the descriptive names for the catalyst "copper–chromium oxide" appears to be the most generally accepted and will be used to designate the normal catalyst in the following discussions. In order to determine its real composition and to investigate its behavior by means of X-ray diffraction a similar study of the pure copper chromites has been necessary.

It is the primary purpose of this paper to report the characteristic powder diffraction data for cupric and cuprous chromites, to clarify the composition of the normal catalyst by means of positive identification of its components through their powder diffraction patterns and to further apply these data to the study of catalyst transformations during use and reclamation. All diffraction work was carried out on G.E. and Norelco apparatus using CuKα radiation.

Cupric Chromite and Cuprous Chromite

Following the Groger[4] method for preparing the copper chromites, separate samples of precipitated chromate were given ignition treatments ranging from one hour at 700° to several hours at 1100°. After each ignition the crystalline product was leached with hot, concentrated hydrochloric acid until cupric ion no longer appeared in the filtrate and the diffraction pattern of cupric oxide could no longer be detected in that of the solid residue.

The washed products which had received the extremes of ignition treatment were found to be single, structurally different, crystalline compounds whose chemical analyses very closely checked those calculated for cupric chromite ($CuCr_2O_4$-low temperature) and cuprous chromite ($Cu_2Cr_2O_4$[5] high temperature), respectively. Tables IB and IC list the diffraction data for these compounds.

From their characteristic diffraction patterns, both chromites were identified in samples which had received intermediate ignition treatment, the cuprous salt systematically replacing the cupric chromite at higher temperatures. Since the unwashed products contained only cupric oxide in addition to the chromites, high temperature interaction of cupric oxide with cupric chromite to give cuprous chromite was indicated. Behavior of this system was determined by an extensive series of ignitions made in air. The three most important typical reactions, determined through positive diffraction identification of all solid components, are discussed below.

(1) Pure cupric chromite prepared by the Groger method was ignited at temperatures increasing from 700 to 1100°. The material was found to be relatively stable at low temperatures but to break down to give cuprous chromite and chromic oxide at high temperatures according to the simplified reaction

$$2CuCr_2O_4 \xrightarrow{>900^\circ} Cu_2Cr_2O_4 + Cr_2O_3 + [O]$$

(2) An intimate equimolar mixture of cupric chromite and cupric oxide behaved quite differently under the above ignition conditions. At temperatures below 900° these components were observed to combine slowly to form only cuprous chromite and oxygen; above 900°, this reaction could readily be driven to completion

$$CuCr_2O_4 + CuO \xrightarrow{>900^\circ} Cu_2Cr_2O_4 + [O]$$

(3) Though the cuprous chromite obtained in the above fashion was found to be entirely stable at room conditions it was completely reoxidized to the original components by "annealing" in air for several hours at temperatures between 600 and 700°. Thus

$$[O] + Cu_2Cr_2O_4 \xrightarrow{600\text{–}700^\circ} CuO + CuCr_2O_4$$

From the second observation the mechanism of formation of cuprous chromite at high temperatures in the Groger synthesis is apparent. Together with the final one these direct diffraction results verify the high temperature equilibrium claimed by L. and P. Wohler[6] from oxygen pressure measurements on a closed system originally containing an equi-molar mixture of cupric oxide and cupric chromite.

$$CuO + CuCr_2O_4 \overset{\text{"red heat"}}{\rightleftarrows} Cu_2Cr_2O_4 + [O]$$

The "Copper-Chromium Oxide" Catalyst

Preparation of the "copper–chromium oxide" catalyst by thermal decomposition of copper am-

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[1] Presented before the Inorganic and Physical Section at the American Chemical Society Meeting, Atlantic City, April, 1947.

[2] "Organic Syntheses," Vol. XIX, John Wiley & Sons, Inc., New York, N. Y., 1939, pp. 31–35.

[3] Adkins, "Reactions of Hydrogen with Organic Compounds," The University of Wisconsin Press, Madison, Wis., 1937.

[4] Groger, *Z. anorg. Chem.*, **58**, 412 (1902); **76**, 30 (1912).

[5] The double formula $Cu_2Cr_2O_4$ will be used instead of $CuCrO_2$ to more directly indicate the oxide composition ($Cu_2O \cdot Cr_2O_3$).

[6] L. and P. Wohler, *Z. physik. Chem.*, **62**, 445–453 (1908).

monium chromate was first described by Adkins and Connor[7] and by Lazier.[8] Many other ways of combining the oxides of copper and chromium have since been tried with varied success in catalytic application[2,3] but the most efficient catalysts have usually been obtained by some modification of the method originally suggested and blocked out below

$$\underset{\text{(Reactants)}}{\mathrm{Cu(NO_3)_2\ soln.} + \mathrm{(NH_4)_2CrO_4\ soln.}} \longrightarrow$$

$$\text{(Intermediate precipitate)}$$

$$\text{Complex chromates} \xrightarrow[\text{decomposition}]{\text{low temperature}} \underset{\text{“Copper–chromium oxide”}}{\text{(Catalyst)}}$$

Connor, Folkers and Adkins[9] early suggested the partial replacement of copper by barium, and Calingaert and Edgar[10] claimed the following near quantitative reactions to describe the two step process.

$$2CuSO_4 + Na_2Cr_2O_7 + 4NH_3 + 3H_2O \longrightarrow 2Cu(OH)NH_4CrO_4 + Na_2SO_4 + (NH_4)_2SO_4 \quad (1)$$

$$2Cu(OH)NH_4CrO_4 \xrightarrow[\text{decomposition}]{\text{Low temp.}} \underset{\text{(Catalyst)}}{Cr_2O_3 \cdot 2CuO} + N_2 + 5H_2O \quad (2)$$

It is possible to carry out the decomposition step under sufficiently controlled low temperatures (350°) to secure "copper–chromium oxide" catalysts which are amorphous. At slightly higher ignition temperatures the presence of a fraction of very small crystallites is indicated by weak and broad diffraction bands. Ordinarily, however, the exothermic nature of the decomposition reaction makes its temperature control difficult and the normal ignited catalyst batch usually is a mixture of completely crystallized components.

Though one cannot determine the composition of amorphous catalysts by X-ray diffraction, it appears significant that only very slight differences in absolute chemical composition between amorphous and crystalline "copper–chromium oxide" catalysts can be detected and that a constant Cu:Cr ratio is maintained. Accordingly it seems reasonable to assume that the component composition of amorphous catalysts may be very similar to that of the crystalline catalysts normally prepared for production applications. Typical behavior of both the simple catalyst prepared according to the directions of Calingaert and Edgar and of the similarly obtained barium-modified catalyst has been determined by X-ray diffraction.

Intermediate Precipitate.—The barium-free intermediate was found to be a single, crystalline material having a chemical composition closely approximating the formula $Cu(OH)NH_4CrO_4$.[10] Partial (10%) replacement of copper by barium caused precipitation of crystalline barium chromate which appeared to remain substantially unchanged during catalyst decomposition, use and reclamation and therefore has been omitted from the discussion of the subsequent steps.

Normal Catalyst.—Decomposition of the above precipitate and ignition at 500° for two hours produced the finely divided, black, crystalline normal catalyst. From its diffraction data cupric oxide and cupric chromite were readily identified and their relative line intensities found to indicate an equimolar ratio. This latter result was closely checked by chemical analyses and is further substantiated by those reported by Calingaert and Edgar in their previous analytical study. Without claiming any such real compound they indicated the catalyst composition to be $Cr_2O_3 \cdot 2CuO$. The true mode of combination determined by the diffraction data is $CuCr_2O_4 + CuO$. Catalyst batches ignited above 600° were found already to show the expected partial combination of cupric oxide with cupric chromite to form cuprous chromite and at very high temperatures (1100°) this conversion was completed.

Used Catalyst.—X-Ray data from catalysts which had been used in a typical liquid phase hydrogenation below 300° often showed crystalline cupric chromite to have been largely reduced to the cuprous chromite in a reaction with cupric oxide competing with the reduction of this oxide to crystalline, metallic copper. The red color of such used catalysts has long been claimed—and is proved by the identifiable diffraction pattern of metallic copper—to be due to the finely divided metal and many empirical attempts have been made to prevent this reduction. The very low temperature reaction of cupric oxide with cupric chromite to produce the cuprous salt has not previously been considered and should be taken into account in further efforts to develop the catalyst and explain its behavior.

Reclaimed Catalyst.—It has been economically feasible to reclaim used "copper–chromium oxide" catalyst by burning off the residual organic materials with alcohol in open pans and reigniting the catalyst for two hours at 600°. Diffraction data from samples taken at various stages of the reclamation process show that the copper is readily reoxidized but that the cuprous chromite remains unchanged. From the previous study of the copper chromites it was apparent that, to obtain a catalyst composition identical with that of new material, a relatively long, low temperature "annealing" treatment would be necessary. A four to six hour annealing at 650° in air was found sufficient to reoxidize the cuprous chromite of the used catalyst to the cupric salt giving a material chemically and structurally identical with the original catalyst.

Summary

The reactions involved in the copper chromite

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(7) Adkins and Connor, THIS JOURNAL, **53**, 1090-1095 (1930).

(8) Lazier, U. S. Patent 1,746,782 (1930).

(9) Connor, Folkers and Adkins, THIS JOURNAL, **53**, 2012 (1931); **54**, 1138 (1932); U. S. Patent 2,091,800 (1937).

(10) Calingaert and Edgar, *Ind. Eng. Chem.*, **26**, 878 (1934).

system may be summarized in a sketch of the following type

$$\begin{tikzcd}
\text{(Precipitate)} & \text{(New catalyst)} & \text{(Annealed catalyst)} \\
2Cu(OH)NH_4CrO_4 \arrow[r, "400\text{–}500^\circ"] & CuO + CuCr_2O_4 \arrow[r, phantom, "="] \arrow[d, "{[H]}"'] & CuO + CuCr_2O_4 \\
& Cu + Cu_2Cr_2O_4 \arrow[r, "+\ {[O]}", "\text{``burn-off''}"'] & CuO + Cu_2Cr_2O_4 \arrow[u] \\
& \text{(Used catalyst)} & \text{(Reclaimed catalyst)}
\end{tikzcd}$$

The Copper Chromite "Spinel"[11]

Cupric chromite has often been spoken of as a likely spinel-former though a careful check of the diffraction literature has failed to turn up data to prove the point. Among the most recent of such assertions are those of Selwood[12] who discussed the "spinel" obtained by high temperature ignition of an oxide mixture and of the "copper–chromium oxide" catalyst. Samples kindly provided by him and thought to be representative of the treatment given his samples no. 16 and no. 17 have been carefully re-examined in this Laboratory by X-ray diffraction methods. The "spinel" prepared by high temperature vacuum ignition of a 1:1 mechanical mixture of copper oxide and chromic oxide is heterogeneous containing free chromic oxide and cuprous chromite; that prepared by high temperature vacuum ignition of the normal copper chromite catalyst is identical in chemical composition and crystalline structure with the cuprous chromite obtained by our similar ignitions in air. These high temperature catalysts do not have the typical spinel composition; furthermore there is strong indication that the cuprous chromite really formed crystallizes on an hexagonal lattice instead of the cubic one required by the spinel structure.

Thin, single crystal plates of the cuprous chromite prepared in this laboratory by high temperature ignition of an equimolar mixture of cupric oxide and cupric chromite are optically isotropic in the plate view, anisotropic in the edge view, show a typical uniaxial interference figure and are characterized by angles of 60 and 120° between bounding edges. Laue data secured from plates mounted perpendicular to the X-ray beam show perfect hexagonal symmetry and axial lengths of the indicated hexagonal cell a_0 = 2.975 Å., c_0 = 17.096 Å. have been calculated from single crystal oscillation and powder back reflection data. A rough density measurement of 7.0 g./cc. by carbon tetrachloride displacement indicates two $Cu_2Cr_2O_4$ per unit cell. All lines of the CuKα powder diffraction pattern of this compound have been successfully indexed on the basis of the hexagonal cell and further work on the single crystal data is in progress.

In the following table are listed the interplanar spacings ("d") and estimated line intensities (I) found to be characteristic of (A) $Cu(OH)NH_4CrO_4$, (B) $CuCr_2O_4$ and (C) $Cu_2Cr_2O_4$, respectively. Line spacings have been approximately corrected for sample absorption and line intensities relate only to the strongest line of each pattern and do not permit direct intercomponent comparison.

Table I

Diffraction Data

(A) $Cu(OH)NH_4CrO_4$ "d"	I	(B) $CuCr_2O_4$ "d"	I	(C) $Cu_2Cr_2O_4$ "d"	I	HK·L
7.1 Å.	100	4.87 Å.	15	5.69 Å.	<5	00·3
4.96	10	3.017	25	2.85	40	00·6
2.69	40	2.874	35	2.570	20	10·0
3.28	55	2.556	100	2.470	100	10·2
2.945	15	2.401	60	2.210	40	10·4
2.737	25	2.134	25	1.911	5	10·6
2.622	20	1.960	10	1.646	45	10·8
2.542	30	1.706	15	1.488	35	11·0
2.365	10	1.629	40	1.439	5	11·3
2.304	20	1.589	15	1.426	30	00·12
1.962	10	1.505	30			10·10
1.848	5	1.442	40	1.319	20	11·6, $\bar{1}$2·6
1.832	5	1.293	5	1.275	15	02·2
1.774	15	1.276	15	1.234	10	02·4
1.645	15	1.195	5			20·6
1.545	10	1.106	5	1.172	<5	10·13
1.483	10	1.067	10			11·9
1.456	5	1.031	<5	1.105	15	10·14
1.383	5	0.985	5			02·8
1.315	<5	.955	10	1.030	20	02·10
1.285	5	.930	<5			11·12, $\bar{1}$2·12
1.143	<5	.885	5	0.988	5	10·16
1.102	5	.857	15	.968	15	21·2, $\bar{1}$3·2
				.949	10	00·18
						21·4, $\bar{1}$3·4
				.886	20	02·14
						21·8, $\bar{2}$3·8
				.858	15	30·0
				.846	20	21·10, $\bar{1}$3·10
				.822	20	02·16
						30·6
				.811	15	10·10
				.801	30	11·18

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Summary

Cupric chromite and cuprous chromite have been prepared, chemically analyzed, characterized by their X-ray powder diffraction data and found to be related in the following way.

$$CuO + CuCr_2O_4 \underset{600\text{–}700^\circ}{\overset{900^\circ}{\rightleftarrows}} Cu_2Cr_2O_4 + [O]$$

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[11] The "Spinel" structure is based upon a face-centered cubic unit cell containing eight R_2MX_4(Cr_2CuO_4 in this case).

[12] P. W. Selwood, F. N. Hill and Harold Boardman, This Journal, **68**, 2055 (1946).

Crystalline $Cu(OH)NH_4CrO_4$ precipitated in the first step of the preparation of "copper-chromium oxide" catalyst, is decomposed at relatively low temperatures to produce an equimolar mixture of cupric oxide and cupric chromite, the normal catalyst. Very high temperature ignition of the catalyst causes their complete combination to form cuprous chromite. Microscopic and X-ray data indicate the latter substance to crystallize in the hexagonal system with two $Cu_2Cr_2O_4$ per unit cell, a_0 = 2.975 Å., c_0 = 17.096 Å.

Normal "copper-chromium oxide" catalysts used in typical low temperature hydrogenations show partial or complete reduction to metallic copper and cuprous chromite. Ordinary reclamation processes succeed only in removing organic matter and re-oxidizing the copper but complete return to the chemical composition of the original catalyst can be accomplished by a relatively long, low temperature "annealing" treatment.

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[CONTRIBUTION FROM INSTITUTT FOR UORGANISK KJEMI, NORGES TEKNISKE HÖGSKOLE]

The Equilibrium $CaCO_{3(melt)} = CaO_{(s)} + CO_2$. The Activity Coefficients of Calcium Carbonate in Alkali Carbonate Melts

BY H. FLOOD, T. FÖRLAND AND B. ROALD

Experimental

The equilibrium diagram of the system calcium carbonate-sodium carbonate-carbon dioxide (p_{CO_2} = 1 atm.) has been examined by P. Niggli,[1] and later by W. Eitel.[2] A sketch of the diagram is shown in Fig. 1a. Only the right-hand side of the diagram is of interest in connection with the questions to be treated here. At the composition ratio 1:1, a compound ($CaCO_3 \cdot Na_2CO_3$) appears which is decomposed at temperatures above 817°. Solid calcium carbonate does not dissolve appreciable amounts of sodium carbonate. The solubility of calcium carbonate in the melt increases with the temperature (compare the curve DA). At about 900° the carbon dioxide tension of solid calcium carbonate exceeds 1 atm. Above this temperature only calcium oxide, not calcium carbonate, can exist in equilibrium with the melt. The composition of the melt in equilibrium with calcium oxide at 1 atm. carbon dioxide pressure is given by the curve AB. The curve AB has been only roughly estimated in the previous publications. Thus in the diagram of W. Eitel it is drawn with the curvature the wrong way.

By assuming calcium oxide insoluble[3] in the melt, however, the curve AB can be determined by a simple gravimetric procedure.

Starting with a melt, for instance, of composition and temperature corresponding to the point N_1, T_1 (compare Fig. 1b), and raising the temperature to T_2, calcium oxide will be precipitated and carbon dioxide expelled until the composition of the melt corresponds to N_2. This composition is given by the amount of carbon dioxide expelled, which is determined by weighing. By further raising of the temperature to T_3 another composition corresponding to N_3 will be found after adjustment of the equilibrium, etc. In this way the curve AB may be determined.

The experiments were carried out in an apparatus previously used in the investigation on the reactions of polyacids with alkali carbonate[4] (compare also ref. 1). As precipitated calcium oxide proved to re-dissolve very slowly in the melts, the experiments were always carried out at rising temperatures.

The platinum crucible with the weighed charge was placed in the heating zone of the furnace and kept there at a constant temperature about twenty minutes. Then it was quickly as possible removed, cooled in a desiccator and weighed (in a weighing bottle).

In addition to the system mentioned, the system with potassium carbonate was examined. Also a few experiments with lithium carbonate were carried out. The results are given in Table I and a graphical representation is shown in Fig. 2. The potassium and sodium systems give results with smaller limits of error than the lithium system. It seems that basic lithium melts may cause an attack on the platinum crucible.

TABLE I

Experiment	Temperature, °C.	Mol. 10^{-3} CaO precip.-CO_2 expelled	$CaCO_3$	K_2CO_3	N_{CaCO_3}
		A. K_2CO_3-$CaCO_3$			
I	20	0	11.10	5.62	(66.4)
	971	3.93	7.12	5.62	55.9
	1078	7.88	3.22	5.62	36.4
II	20	0	6.18	3.47	(64.0)
	1008	2.93	3.25	3.47	47.9
	1063	3.91	2.27	3.47	39.5
	1105	4.43	1.75	3.47	33.5
		B. Na_2CO_3-$CaCO_3$			
I	20	0	9.18	9.04	(50.4)
	964	1.60	7.58	9.04	45.6
	1044	5.67	3.51	9.04	28.0
II	20	0	9.68	8.47	(53.3)
	1005	5.01	4.67	8.47	35.5
	1097	7.52	2.16	8.47	20.3
		C. Li_2CO_3-$CaCO_3$			
I	20	0	7.00	12.04	(36.8)
	971	1.35	5.65	12.04	32.0
	1034	4.23	2.77	12.04	18.7
II	20	0	8.36	13.57	(38.1)
	1018	4.19	4.17	13.57	23.5

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(1) P. Niggli, *Z. anorg. Chem.*, **98**, 241 (1916).

(2) W. Eitel, *Tschermak's Min. Petr. Mitt.*, **38**, 1 (1925).

(3) A correction can be made for the solubility of calcium oxide in the melt by examining the amount of expelled carbon dioxide at temperatures and compositions just below the curve AB. The experiments indicated that the correction was negligible.

(4) H. Flood, T. Förland and B. Roald, unpublished.