

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

## THE PREPARATION OF COPPER-CHROMIUM OXIDE CATALYSTS FOR HYDROGENATION

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The copper-chromium oxide catalyst which recently has been found to be so effective in the hydrogenation of various organic compounds<sup>1</sup> in the liquid phase was originally prepared by the decomposition of a precipitated copper ammonium chromate. The process for the preparation of the catalyst was that used by Lazier<sup>2</sup> for the preparation of zinc and manganese "chromite" catalysts for the hydrogenation of carbon monoxide in the vapor phase.

The utilization of this catalyst soon raised a number of questions in regard to its preparation. In attempting to answer some of these questions a very considerable number of catalysts containing copper and chromium have been prepared by various procedures. In order to bring some semblance of order into the presentation of a rather empirical investigation the modifications in the ingredients and procedures for the preparation of catalysts will be considered under three heads: (1) the improvement of the method for the preparation of a catalyst through the decomposition of copper ammonium chromate; (2) the promotion and stabilization of the activity of copper chromium oxide catalysts by the addition of another metal to the catalyst; (3) the development of methods, other than the decomposition of the chromates, for the preparation of copper-chromium oxide catalysts.

**Testing the Activity of Catalysts.**—The copper-chromium oxide catalysts described in this paper were tested under arbitrarily chosen conditions and they are compared on the basis of the results obtained. It is realized fully that if the catalyst had been tested in the hydrogenation of other compounds under different conditions of temperature, pressure, ratio of catalyst, etc., the relative merits of the catalyst might have been different. It was recently pointed out<sup>3</sup> that even the relative activity of two preparations of catalyst was a function of the particular set of experimental conditions (hydrogen acceptor, temperature, hydrogen pressure, amount of catalyst, ratio of catalyst to hydrogen acceptor, thoroughness of dispersion of catalyst in reaction mixture, etc.) used in testing the activity. It was also indicated that catalysts for hydrogenation

<sup>1</sup> Adkins, Connor and Folkers, *THIS JOURNAL*, **53**, 1091, 1095 (1931).

<sup>2</sup> Lazier, British Patent 301,806, January 12, 1926; U. S. Patent 1,746,783, February 11, 1930.

<sup>3</sup> Adkins and Covert, *J. Phys. Chem.*, **35**, 1684 (1931).

may have several different characteristics any one of which may serve as a basis of comparison.

Acetone, furfural, ethyl  $\beta$ -phenylpropionate, ethyl phenylacetate, ethyl hexahydrobenzoate and spermaceti (*i. e.*, crude cetyl palmitate) have been used to test the activity of these catalysts. These compounds were selected on the basis of the following considerations. Acetone is very readily hydrogenated, so it is a suitable compound for testing rather inactive catalysts. If a catalyst will not induce the hydrogenation of acetone, it is indeed a poor catalyst. If a catalyst was found to be rather inactive toward acetone it was not in general tested against the more difficultly hydrogenated compounds. Furfural is not so readily hydrogenated as acetone, and so it imposes a more severe test on a catalyst. The hydrogenation of the esters to the corresponding alcohols involves a hydrogenation distinctly different from that in the hydrogenation of aldehydes and ketones and requires a much higher temperature and a more stable catalyst.  $\beta$ -Phenylpropionic and hexahydrobenzoic esters and spermaceti were selected because of their availability and because their hydrogenation is typical of a large number of esters. Phenylacetic ester was used because it offers further complications in that the alcohol ( $\beta$ -phenylethyl) is readily hydrogenated to ethylbenzene.

**Activity of Catalysts from Copper Ammonium Chromate.**—The procedure for the preparation of a catalyst by the decomposition of an ammonium chromate given for catalysts 25 and 36 KAF and 28 RAC is one which was gradually developed in this Laboratory. It has been repeated many times and has been found to give uniformly excellent results.

**Preparation of Catalysts from Copper-Barium-Ammonium Chromates (25,36 KAF, 28 RAC).**—Nine hundred ml. of a solution (80°) containing 261 g. of hydrated copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) and 31.3 g. of barium nitrate was added to 720 ml. of a solution (25–30°) containing 151.2 g. of ammonium dichromate and 150 ml. of 28% ammonium hydroxide. The precipitate was filtered, the cake being pressed with a spatula and sucked as dry as possible. After drying in an oven at 75–80° overnight, and pulverizing, the product weighed 234 g. It was decomposed in three portions in a casserole over a free flame. In carrying out the decomposition, the powder was stirred with a spatula from the beginning of the heating, and the flame was removed after the decomposition was well started. After a little more stirring, there was a sudden evolution of gases and the entire mass became black. After another thorough stirring the powder was removed from the hot casserole and allowed to cool. The combined product was then leached for thirty minutes with 600 ml. of 10% acetic acid solution, filtered, and washed with 600 ml. of water in six portions, dried overnight at 125°, and pulverized. The product weighed 149.5 g.

The activity of the catalysts so prepared is evidenced by the fact that 3 g. of catalyst No. 25 KAF induced rather rapid hydrogenation of 75 g. of furfural under a pressure of  $163 \pm 27$  atmospheres of hydrogen, at a temperature of  $130\text{--}135^\circ$ . The furfural was completely hydrogenated to tetrahydrofurfuryl alcohol within about ten minutes as the bomb was heated up to  $160\text{--}165^\circ$ . The hydrogenation was complete within four minutes after the temperature of the bomb reached  $160^\circ$ . Five grams of this catalyst brought about the complete hydrogenation of 0.25 mole of ethyl hexahydrobenzoate at  $250^\circ$  within fifty-two minutes. Further washing of the catalyst with 20% acetic acid enhanced its activity so that the time required for the hydrogenation of the ester was reduced to thirty minutes. Heating the catalyst to  $400^\circ$  for two minutes did not decrease its activity.

Both the amount and activity of the catalyst obtained in a given preparation were found to vary with the quantity of ammonium hydroxide used for the precipitation of the copper ammonium chromate. A series of catalysts (31, 32, 33 and 34 KAF) were made on one-third the scale of No. 25 KAF, in which the amount of ammonium hydroxide used was variously 125, 75, 50 and 20 ml. When these catalysts were tested on furfural, under the conditions noted above, 101, 0.5, 23 and 45 minutes were required for complete hydrogenation after the temperature of the bomb reached  $160^\circ$ . The proportion of ammonium hydroxide used in preparing catalyst No. 32 KAF was the most advantageous not only because it gave the most active catalyst but also because it gave a considerably larger yield of catalyst. In washing this series of catalysts a 40% solution of acetic acid was tried instead of the 10% solution used in the procedure for catalyst 25 KAF. This more drastic washing of the catalyst was quite satisfactory in the smaller scale of operation used in preparing catalysts 31, 32, 33 and 34 KAF but when it was used on the triple scale of 35 KAF a rather poor catalyst was obtained. The procedure given for catalyst No. 37 KAF is a combination of the procedures for 25 and 32 KAF and represents the best method so far found for the preparation of a copper-chromium-barium oxide catalyst. When this catalyst was tested on furfural, as described above, hydrogenation was complete in two minutes after the temperature of the bomb reached  $160^\circ$ .

Catalyst 37 KAF was prepared as follows. Nine hundred ml. of a solution ( $80^\circ$ ) containing 261 g. of hydrated copper nitrate and 31.3 g. of barium nitrate was added to 900 ml. of a solution ( $25\text{--}30^\circ$ ) containing 151.2 g. of ammonium dichromate and 225 ml. of 28% ammonium hydroxide. The procedure from this point was the same as that given for 25 KAF. The yield of catalyst was 170 g.

Catalysts which contained cadmium (27 KAF) or silver (30 KAF) in addition to copper, barium and chromium were not particularly active.

Ethyl hexahydrobenzoate (0.25 mole) with 5 g. of catalyst was completely reduced at 250° within 210 minutes by 27 KAF and in 113 minutes by 30 KAF. The former catalyst was made through the precipitation of the carbonate with sodium bicarbonate while the latter was made by the dichromate method.

**The Stabilization and Promotion of the Activity of Copper-Chromium Oxide Catalysts.**—The active catalysts containing copper which have been used in this Laboratory are all black or dark brown in color and apparently contain the copper in the divalent state. These dark colored catalysts are under some conditions reduced to reddish colored compounds. This reduction of the copper from the divalent to the monovalent or elementary state occurs for example at 360° when ethanol is passed over the catalyst. The reduction also occurs in the presence of certain more easily oxidized compounds at temperatures as low as 150 to 175°. The resulting reddish copper compound is rather inactive for hydrogenation although it has a high catalytic activity for some other types of reaction as, for example, the conversion of aldehydes into esters.

It has been found advantageous to have barium,<sup>4</sup> calcium or magnesium compounds present in the copper-chromium oxide catalyst in order to retard or inhibit reduction of the catalyst. For example, two samples of catalyst prepared in the same way, but one containing only copper and chromium (20 RAC) and the other containing barium, copper and chromium (22 RAC), were tested against ethyl caprylate. The one containing barium induced 90% hydrogenation of the ester after 7.25 hours and was black in color when it was removed from the reaction mixture. The catalyst which contained no barium failed to bring about any appreciable hydrogenation of the ester and was bright red in color when it was removed from the ester. These two catalysts showed very little difference in the rate at which they catalyzed the hydrogenation of acetone and furfural; thus it appears that the effect in the case of the ester was not so much to promote the activity of the catalyst as it was to stabilize it against reduction.

The necessity for the incorporation of barium, calcium or magnesium in the catalyst varies with the ester and with its purity, and also with the proportion of ester to catalyst used. If a high ratio of a very active catalyst is used, then the hydrogenation may be complete before the catalyst is reduced.

The effect of the presence of calcium as a component of the catalyst is indicated by the results obtained in the hydrogenation of ethyl  $\alpha$ -phenylbutyrate. Under identical conditions a catalyst (18 KAF) containing only copper and chromium required 36 minutes for the hydrogenation of this ester, while a catalyst (39 KAF) which contained calcium

<sup>4</sup> Cf. Connor, Folkers and Adkins, *THIS JOURNAL*, 53, 2012 (1931).

brought about the hydrogenation in five minutes. The ratio of the products was almost the same, *i. e.*, 1 to 3% residual ester, 15 to 19% hydrocarbons and 78 to 79% 2-phenylbutanol-1. The addition of magnesium or calcium to a copper-chromium oxide reduced the time for the hydrogenation of ethyl phenylacetate to approximately 35% of that required by the simpler catalyst. The introduction of an additional component to the copper-chromium oxide catalyst not only appears to stabilize the catalyst against reduction and to enhance the activity but also modifies the ratio of the product formed in the hydrogenation of such a compound as ethyl phenylacetate. The ratio of ethylbenzene to phenylethyl alcohol for calcium being 1 to 6 and for magnesium 1 to 2. The complete data in support of these statements is given in Table I of the accompanying paper on hydrogenation of esters.

**Preparation of Catalysts Containing Magnesium, Calcium and Strontium.**—Catalysts 38, 39 and 40 KAF containing magnesium, calcium and strontium, respectively, were prepared on one-third the scale but in the same manner as 25 KAF, except that 10.3 g. of magnesium nitrate hexahydrate, 6.6 g. of calcium nitrate or 8.5 g. of strontium nitrate was substituted for the barium nitrate. The weights of product were 34, 38 and 36 g., respectively.

**The Preparation of Copper Oxide Catalysts Other than Through the Decomposition of the Chromates.**—Data on the activity of eighteen catalysts prepared otherwise than by the decomposition of copper ammonium chromate have been summarized in Table I. It is apparent that all the products which contained divalent copper catalyzed hydrogenation, while the one which contained cuprous copper was inactive. Cupric oxide alone (14 RAC—prepared by decomposition of copper oxalate) catalyzed the hydrogenation of acetone, but a temperature of 200° was necessary for very rapid hydrogenation and the catalyst was in the red form after the run. The presence of chromium oxide (21 RAC—prepared by mixing the copper oxalate with ammonium dichromate before the decomposition) caused the hydrogenation of acetone as rapidly at 150° as the copper oxide had done alone at 200°. This catalyst was black after the run. The desirability of mixing the components before decomposition is shown by a comparison of catalysts 21 RAC and 33 RAC made by the same procedure except that in one case the copper oxalate and ammonium chromate were mixed before decomposition, and in the other these components were decomposed separately and then mixed. The latter method gave a much inferior catalyst.

Copper oxide (Mallinckrodt's) was superior to that prepared from the oxalate (33 RAC and 26 RAC). It seemed to make no difference, however, whether commercial Cr<sub>2</sub>O<sub>3</sub> was used or whether this oxide was prepared by decomposition of ammonium dichromate (23 RAC and 26 RAC; 23a RAC and 26a RAC).

TABLE I

CATALYTIC ACTIVITY OF VARIOUS COPPER OXIDE CATALYSTS AT 150-250 ATMOSPHERES

Source of catalyst <sup>e</sup>	Catalyst No.	Acetone <sup>a</sup>	Furfural <sup>b</sup>	Esters
Copper oxalate	14 RAC	14 m. (200°)		
CuO <i>ex</i> oxalate + Cr <sub>2</sub> O <sub>3</sub> <i>ex</i> (NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	33 RAC	300 m. (175°)		
Copper oxalate + (NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	21 RAC	13 m. (150°)		
Copper oxalate + (NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> + BaCrO <sub>4</sub>	27 RAC			50% (10.5 hrs.) <sup>f</sup>
Cu, Cr, Ba oxalates (coppt.)	25 RAC		20 m. (160°)	66% (11.5 hrs.) <sup>c</sup>
Mixture of CuO + Cr <sub>2</sub> O <sub>3</sub>	23 RAC	75 m. (175°)		
Mixture of CuO + Cr <sub>2</sub> O <sub>3</sub> (5 m. at 450°)	23a RAC	30 m. (175°)		
Mixture of CuO + Cr <sub>2</sub> O <sub>3</sub> <i>ex</i> (NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	26 RAC	70 m. (175°)		
Mixture of CuO + Cr <sub>2</sub> O <sub>3</sub> <i>ex</i> (NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (5 m. at 450°)	26a RAC	20 m. (175°)		
Mixture of CuO + Cr <sub>2</sub> O <sub>3</sub> <i>ex</i> (NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (1 hr. at 450°)	26b RAC	45 m. (175°)		
Mixture of CuO with BaO and Cr <sub>2</sub> O <sub>3</sub> <i>ex</i> BaCrO <sub>4</sub> and (NH <sub>4</sub> ) <sub>2</sub> - Cr <sub>2</sub> O <sub>7</sub>	32 RAC			85% (7.2 hrs.) <sup>d</sup>
CuO + BaCrO <sub>4</sub> + (NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	24 RAC		120 m. (160°) 50 m. (175°)	85% (12 hrs.) <sup>c</sup>
Cu, Cr, NH <sub>4</sub> carbonates (coppt.)	20 RAC	12 m. (150°)	80 m. (160°)	
Cu, Cr, Ba, NH <sub>4</sub> car- bonates (coppt.) (0.5 as much Cu as 30 RAC)	22 RAC	11 m. (150°)	90 m. (160°)	36% (11 hrs.) <sup>c</sup>
Cu, Cr, Ba, NH <sub>4</sub> car- bonates (coppt.)	30 RAC		5 m. (160°)	100% (2 hrs.) <sup>d</sup>
Cu, Cr, Ba nitrates	31 RAC	20 m. (150°)	105 m. (160°)	100% (3.5 hrs.) <sup>d</sup>
Cu + CrO <sub>3</sub>	34 RAC		175 m. (160°)	
Cu <sub>2</sub> O + Cr <sub>2</sub> O <sub>3</sub>	35 RAC	No activity (200°)		

<sup>a</sup> 58 g. acetone, 1.9 g. of catalyst. <sup>b</sup> 75 g. furfural, 3.0 g. of catalyst. <sup>c</sup> 75 g. of spermaceti, 5 g. of catalyst at 250°. <sup>d</sup> 30 g. of ethyl  $\beta$ -phenylpropionate, 4 g. of catalyst at 250°. <sup>e</sup> A detailed description of the preparation of all of these catalysts was given in the original manuscript submitted to the Editor but due to the necessity for the economy of space these descriptions have been eliminated from the published paper. The catalysts *ex* oxalates, dichromates, carbonates and nitrates were prepared by the decomposition of these salts in the manner described in detail for catalysts 25 KAF and 30 RAC. The preparation of oxide catalysts by the decomposition of oxalates was patented by Lazier (U. S. Patent 1,746,781, February 11, 1930). However, the method was used in this Laboratory for the preparation of copper oxide some years earlier [Adkins and Lazier, THIS JOURNAL, 46, 2295 (1924)].

The catalyst (30 RAC), made by coprecipitation of copper, barium and chromium carbonates, is very distinctly superior to the other catalysts listed in Table II, and is similar in activity to the better catalysts from the chromate. Aside from pointing out the distinct superiority of the carbonate catalysts over the others listed in Table II, it is not felt that the data at hand is sufficient to warrant a decision as to the relative activities of catalysts resulting from other methods of preparations. A change in the quantities of materials used, variations in technique (such as thoroughness of mixing or drying), etc., may cause a marked difference in the activity of the product. It is quite likely that all of the procedures used in the preparation of these catalysts could be modified so as to give more active catalysts. An extensive and precise comparison of the various procedures for the preparation of copper-chromium oxide catalysts is beyond the scope of this work. The salient conclusion that emerges from the data in Table I is that copper-chromium oxide catalysts active for hydrogenation may be prepared by numerous and varied ways, with or without coprecipitation. Even the simplest catalyst—made by grinding together the oxides of copper, chromium and barium and heating them at  $450^{\circ}$  for five minutes (32 RAC)—catalyzed the hydrogenation of ethyl  $\beta$ -phenylpropionate to  $\gamma$ -phenylpropanol.

**Preparation of a Catalyst (30 RAC) from Copper-Barium-Ammonium Carbonates.**—Solutions of the three metallic nitrates were prepared separately as follows: 5.4 g. of barium nitrate ( $\text{Ba}(\text{NO}_3)_2$ ) in 50 ml. of boiling water, 77.2 g. of hydrate of chromium nitrate ( $\text{Cr}_2(\text{NO}_3)_6 \cdot 15\text{H}_2\text{O}$ ) in 450 ml. of warm water, 100 g. of hydrated copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) in 150 ml. of water. The three solutions were mixed ( $35^{\circ}$ ) and 94.4 g. of ammonium carbonate ( $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ) in 535 ml. of water was added. There was a considerable amount of effervescence and a very voluminous precipitate was formed. The precipitate was filtered with suction, washed twice with 50 ml. portions of water, dried at  $110$ – $120^{\circ}$ , pulverized and decomposed in two portions at  $190$ – $230^{\circ}$ . The product was then suspended in 100 ml. of a 10% solution of acetic acid, filtered, washed with two 75 ml. portions of water and dried at  $110$ – $120^{\circ}$ . The product weighed 57 g.

### Summary

The procedure for the preparation of copper-chromium oxide catalysts by the precipitation and decomposition of copper ammonium chromate has been modified and improved so that much larger yields of a considerably more active catalyst may now be obtained.

It has been shown to be advantageous to incorporate barium, calcium or magnesium into the copper-chromium oxide catalyst. The addition of one of these elements stabilizes the catalyst against reduction and consequent deactivation and apparently enhances its activity. These elements also

modify the relative rates of competitive hydrogenations such as are encountered in the preparation of phenylethyl alcohol from ethyl phenylacetate so that larger yields of the alcohols were obtained. The procedure for the preparation of the most active catalysts containing barium is that described for the catalyst labeled 37 KAF, while the most active catalyst yet prepared is that containing calcium and is labeled 39 KAF.

Copper-chromium oxide catalysts have also been prepared by the decomposition of oxalates, by the mechanical mixture of copper and chromium oxides, by the decomposition of their nitrates, by the combination of copper and chromic oxide and by the decomposition of the precipitated copper, chromium, ammonium carbonates. All the products which contained divalent copper catalyzed hydrogenation. The most active catalysts (30 RAC) from this group were prepared by the decomposition of coprecipitated copper, chromium, barium, ammonium carbonates. Such a catalyst was similar in activity to the better catalysts obtained by the decomposition of the corresponding chromates.

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## THE CATALYTIC HYDROGENATION OF ESTERS TO ALCOHOLS. II

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The catalytic hydrogenation over copper-chromium oxide of the carboxy to the carbinol group in 80-98% yields for seven esters was recently described.<sup>1</sup> Because of the utility of this process for the reduction of an ester to the corresponding alcohol, several of the variables involved have been studied further, and the method has been extended to other types of esters, over modified and improved copper-chromium oxide catalysts. This paper, then, is a summary of the significant results of all these experiments. The apparatus and procedure were the same as those previously described.<sup>2</sup>

In Table I there is recorded a summary of the data obtained on the hydrogenation of various esters at 250° and under a pressure of 200 to 300 atmospheres. Table II contains the data on the rates of hydrogenation of

<sup>1</sup> Adkins and Folkers, *THIS JOURNAL*, **53**, 1095 (1931). Since the publication of this paper and the completion of most of the experimental work described herewith, there have appeared three publications describing the hydrogenation of a few acids and esters of high molecular weight to alcohols. Schrauth, Schenck and Steckdorn, *Ber.*, **64**, 1314 (1931); Norman, *Z. angew. Chem.*, **44**, 714 (1931); Otto Schmidt, *Ber.*, **64**, 2051 (1931).

<sup>2</sup> Adkins and Cramer, *THIS JOURNAL*, **52**, 4349 (1930).