Dehydrogenation of Secondary Alcohols with Reduced Copper. IV[1]. *Catalytic Dehydrogenation of Isopropyl Alcohol (Part 2)**

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As has already been pointed out in the preceding paper[1], the activity and the selectivity of various copper catalysts depend not only upon the reaction temperature at which the catalysts are employed, but also on the precipitants in the preparation of the copper catalysts. For instance, the catalyst prepared with potassium bicarbonate shows the greatest activity for dehydrogenating isopropyl alcohol to acetone with no side reaction, while the copper catalyst prepared with sodium hydroxide under the same condition shows the smallest dehydrogenating activity, producing condensation products.

Earlier, Audibert and Raineau[2] reported that a highly active catalyst for the decomposition of methanol was obtained by adding a solution of alkali hydroxide to a boiling solution of copper nitrate, and reducing the black precipitate with hydrogen, and that the catalyst prepared from the oxide precipitated with ammonia from a cold copper nitrate solution was totally inactive for the same reaction. On the other hand, Frolich et al.[3] prepared copper catalysts from the precipitates obtained by adding ammonia to a solution of copper nitrate at various temperatures (0, 10, 22, 55, 85 and 100°C), and found that the greatest activity for the decomposition of methanol was achieved with the precipitate at 22°C. Thus there is non-conformity in the results obtained by various workers.

The present author found that dehydrogenation of isopropyl alcohol at 220∼250°C with the copper catalysts prepared with alkali hydroxide gives oily products (isobutyl methyl ketone and diisobutyl ketone) in addition to acetone, and that the copper catalyst prepared with potassium hydroxide gives a smaller yield of the oily products than that prepared with sodium hydroxide under the same condition[1]. The present investigation was undertaken to confirm this unexpected behavior of the copper catalyst prepared with sodium hydroxide, and to study the effect of the precipitation temperature on the amounts of acetone and the oily products to find a preparation procedure of the most suitable copper catalyst for the production of acetone, precipitation being carried out at 5, 22, 55 and 90°C[4].

It was presumed in the preceding paper that the formation of isobutyl methyl ketone is due to the condensation of the isopropyl alcohol and acetone produced. In order to confirm this formation process, and to determine whether a large quantity of the oily products could be formed from a mixture of isopropyl alcohol and acetone, various mixtures of the alcohol and acetone were passed over the copper catalyst prepared with sodium hydroxide at 22°C.

Experimental

Purification of Isopropyl Alcohol and Acetone.—Isopropyl alcohol and acetone were purified as in the preceding paper. Isopropyl alcohol: b. p. 82∼82.5°C, n_D^{25} 1.3753, d_4^{25} 0.7811. Acetone: b. p. 56.2∼56.3°C, n_D^{25} 1.3564, d_4^{25} 0.7844.

TABLE I. PREPARATION OF PRECIPITATES

Catalyst	Temperature of precipitation °C	Time of drying hr.	Color
Cu VI	5	24	dark gray
Cu VII	22	20	dark gray
Cu VIII	55	20	black

TABLE II. PREPARATION OF PRECIPITATES

Catalyst	Precipitant and amount g.	Distilled water ml.	Time of drying hr.	Color
Cu IX	K_2CO_3, 25	500	10	green
Cu X	$KHCO_3$, 40	400	10	green
Cu XI	$Ba(OH)_2$, 57	1000	20	dark gray

TABLE III. PREPARATION OF PRECIPITATES

Catalyst	Precipitant and amount g.	Distilled water ml.	Time of drying hr.	Color
Cu XII	NaOH, 15	300	20	dark gray
Cu XIII	K_2CO_3, 25	500	10	green
Cu XIV	$KHCO_3$, 40	400	10	green

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1) Part III. This Bulletin, 34, 161 (1961).

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2) E. Audibert and A. Raineau, *Ind. Eng. Chem.*, 20, 1105 (1928).

3) P. K. Frolich, M. R. Fenske and D. Quiggle, *J. Am. Chem. Soc.*, 51, 61 (1929).

4) The case of 90°C was described in the preceding paper[1].

Preparation of Catalysts.—Cupric nitrate hexahydrate was prepared from electrolytic copper and nitric acid, and was purified by recrystallization. The catalysts were prepared as shown in Tables I, II and III. Precipitates for catalysts Cu VI∼Cu VIII (Table I) were prepared as follows: A solution of 30 g. of cupric nitrate hexahydrate in 900 ml. of distilled water was heated or cooled to the temperature chosen for precipitation. A sodium hydroxide solution, prepared from 15 g. of sodium hydroxide and 300 ml. of distilled water, was brought to the same temperature and added rapidly to the copper nitrate solution with stirring. After the mixture was stirred at the same temperature for 30 min., the precipitate was washed well by decantation with distilled water at the same temperature, collected on a glass filter, dried in an electric oven at 105°C for the time given in the table, powdered in an agate mortar, and stored in a stoppered bottle. Precipitates for Cu IX∼Cu XI (Table II) were prepared by the same method as for Cu VII except for the precipitants and the volume of distilled water to dissolve them. Precipitates for Cu XII∼Cu XIV (Table III) were prepared by the following method: Thirty grams of cupric nitrate hexahydrate was dissolved in 600 ml. of distilled water, and 300 ml. of ethyl alcohol was then added. To the solution kept at 22°C a solution of the precipitant dissolved in distilled water as shown in Table III was added, and the precipitate was treated similarly.

Apparatus and Procedure. — The apparatus was exactly the same as that described in the preceding paper. A definite amount (10 g.) of the precipitate was placed in the reaction tube and reduced by passing hydrogen (750∼900 ml./hr.) at a temperature below 185°C. The resulting catalyst was then heated to the operating temperature. Experiments were usually performed at 185, 220, 250, 305 and 325°C under the ordinary pressure, and isopropyl alcohol and the various mixtures of isopropyl alcohol and acetone were passed through the tube, respectively, at a constant rate of flow. The liquid product was collected by the method similar to that described in the preceding paper. The volume of the noncondensable gas evolved by the reaction was measured at intervals of 15∼30 min., and the change in catalytic activity was denoted by the volume. All values given in the present research are averages of three to four measurements under a constant operating condition.

Analysis of the Products. — The reaction mixture was treated with water to remove the acetone and unchanged isopropyl alcohol. The content of acetone in the aqueous solution was determined by the hydroxylamine method. The oily products obtained in some of the experiments were dried with anhydrous sodium sulfate and fractionally distilled, and the constituents of the cuts were identified by boiling points, densities, refractive indices, 2,4-dinitrophenylhydrazones and semicarbazones. The oily products were found to consist mainly of isobutyl methyl ketone and diisobutyl ketone.

Results

Influences of the Temperature of Precipitation and That of Reaction on the Dehydrogenating Activity of Reduced Copper.—The influences of the temperature of precipitation and that of reaction on the activity of copper catalysts are shown in Table IV. The amounts of reaction products given in Tables IV∼VII are reproducible within 1%. Experiments were carried out under controlled conditions in order to eliminate so far as possible effects[5] other than that of the temperature of precipitation or reaction. Table IV indicates that the dehydrogenating activity to give acetone and the condensing activity to give isobutyl methyl ketone and diisobutyl ketone depend on the temperatures of precipitation and of the reaction. As the catalytic activity for the dehydrogenation of isopropyl alcohol varied irregularly with the precipitation temperature, it is impossible to find any simple relation between them. The highest dehydrogenation activity is obtained with the catalyst (Cu VIII) precipitated at 55°C. On the other hand, the yield of the oily products is the highest with the catalyst (Cu VII) precipitated at 22°C. As the dehydrogenating activity of reduced copper varies with the precipitation temperature, it is necessary to fix the precipitation temperature to get the constant activity.

In Fig. 1, the yield of acetone with various specimens of reduced copper is plotted against the reaction temperature. The yield of acetone

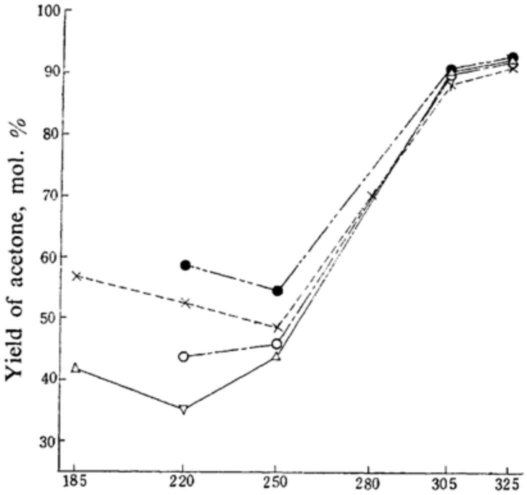

Fig. 1. The effect of temperature on the dehydrogenation of isopropyl alcohol with various copper catalysts.

○ Cu VI, △ Cu VII, ● Cu VIII, × Cu I (described in the preceding paper).

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[5] Those from the reducing condition of precipitates with hydrogen and the velocity of passing the substance over reduced copper.

TABLE IV. INFLUENCES OF THE TEMPERATURE OF PRECIPITATION AND THAT OF REACTION ON THE DEHYDROGENATING ACTIVITY OF COPPER CATALYSTS

Catalyst	Temp. °C	Isopropyl alcohol g.	Velocity g./hr.	Acetone g.	Oily products g.	Gases collected l.	Percentage of conversion %
Cu VI	220	39.38	11.53	16.66	11.58	8.85	60.2
	250	39.28	13.46	17.42	12.31	9.42	64.3
	305	39.36	11.52	34.31	0	13.69	93.2
	325	39.31	11.79	35.12	0	14.08	96.0
Cu VII	185	38.96	11.69	15.72	5.47	7.35	50.5
	220	38.93	11.39	13.24	15.29	8.19	56.4
	250	38.83	11.65	16.48	13.40	9.11	62.9
	280	39.19	11.47	32.22	0.67	13.01	89.0
	305	39.02	11.15	34.21	0	13.78	94.7
	325	38.95	11.40	34.94	0	14.04	96.6
Cu VIII	220	38.70	12.55	21.98	4.14	9.79	67.8
	250	39.21	11.48	20.72	9.69	10.28	70.3
	305	38.72	12.56	34.14	0	13.60	94.2
	325	38.90	11.67	35.04	0	13.95	96.2

TABLE V. INFLUENCE OF PRECIPITANTS ON THE DEHYDROGENATING ACTIVITY OF REDUCED COPPER

Catalyst	Temp. °C	Isopropyl alcohol g.	Velocity g./hr.	Acetone g.	Oily products g.	Gases collected l.	Percentage of conversion %
Cu IX	185	39.36	10.99	19.86	0	7.90	53.8
	220	39.24	11.48	27.67	0	10.99	75.1
	250	39.24	11.48	32.36	0	12.80	87.5
	280	39.32	11.51	34.24	0	13.55	92.4
	305	39.36	11.81	35.54	0	14.05	95.7
	325	39.34	11.80	36.00	0	14.11	96.2
Cu X	185	39.21	11.20	19.80	0	7.88	53.9
	220	39.26	11.49	27.43	0	10.85	74.1
	250	39.30	10.97	31.41	0	12.38	84.5
	305	39.24	11.21	35.17	0	13.77	94.1
	325	39.40	11.53	35.96	0	14.19	96.6
Cu XI	220	38.77	13.29	16.35	12.59	9.00	62.2
	250	38.68	11.16	15.72	13.58	8.90	61.7

increases rapidly with the rising reaction temperature, becoming almost quantitative at 325°C, but is reduced by the formation of considerable amounts of the oily products at lower temperatures.

Influence of Precipitants on the Dehydrogenating Activity of Reduced Copper. — Comparison of Tables IV and V shows that Cu IX and Cu X, obtained by using potassium carbonate and potassium bicarbonate respectively as precipitants, gave the highest yield of acetone at the highest temperature as far as the experiments were performed. These copper catalysts act only to dehydrogenate isopropyl alcohol to acetone at all temperatures, while the catalysts prepared with sodium hydroxide act similarly at the higher temperatures but act on isopropyl alcohol at the lower temperatures not only to dehydrogenate it to acetone but also to produce isobutyl methyl ketone and diisobutyl ketone. The catalyst prepared with barium hydroxide behaves at the lower temperatures similarly to those prepared with sodium hydroxide.

The precipitate prepared with potassium carbonate at 90°C was dark brown, and the catalyst prepared from it gave isobutyl methyl ketone and diisobutyl ketone together with acetone[1].

Use of Isopropyl Alcohol and Acetone as Starting Materials.—Investigation was made as to whether or not the amount of the oily products is changed by adding acetone to isopropyl alcohol in the charge. The results summarized in Table IV show that acetone mixed beforehand does not essentially participate in the production of isobutyl methyl ketone and diisobutyl ketone.

Influence of the Addition of Ethyl Alcohol to Copper Nitrate Solution. — Investigation was made as to whether or not the dehydrogenating activity of reduced copper could be

TABLE VI. THE EFFECT OF THE RATIOS OF ISOPROPYL ALCOHOL TO ACETONE ON THE YIELD OF OILY PRODUCTS

Acetone g.	Isopropyl alcohol g.	Temp. °C	Velocity g./hr.	Acetone in reaction product g.	Oily products g.	Gases collected l.	Percentage of conversion %
38.82	0	220	12.59	37.54	0	0.17	—
38.98	0	250	12.64	37.72	0	0.17	—
31.93	7.71	220	12.52	34.26	—	1.63	56.6
19.50	19.70	220	12.71	25.44	5.06	3.87	52.7
7.68	31.45	220	11.45	21.04	8.08	7.04	60.0
0	38.93	220	11.39	13.24	15.29	8.19	56.4
0	38.83	250	11.65	16.48	13.40	9.11	62.9

TABLE VII. INFLUENCE OF THE ADDITION OF ETHYL ALCOHOL TO COPPER NITRATE SOLUTION

Catalyst	Temp. °C	Isopropyl alcohol g.	Velocity g./hr.	Acetone g.	Oily products g.	Gases collected l.	Percentage of conversion %
Cu XII	220	39.07	10.90	13.91	15.10	8.38	57.5
	250	38.95	11.68	16.73	13.42	9.20	63.3
	305	39.06	11.72	34.89	0	13.83	94.9
	325	39.03	11.71	35.57	0	14.08	96.7
Cu XIII	220	39.30	10.97	25.92	0	10.21	69.6
	250	39.33	10.98	31.37	0	12.35	84.2
	305	39.33	11.80	35.76	0	13.96	95.1
	325	39.19	10.94	36.35	0	14.23	97.3
Cu XIV	220	38.97	12.64	16.28	0	6.56	45.1
	250	39.05	12.33	26.57	0	10.39	71.3
	305	39.08	11.44	33.70	0	13.35	91.6
	325	39.06	11.43	35.59	0	14.03	96.3

increased by the addition of ethyl alcohol in the preparation of the precipitate. The results are shown in Table VII. Comparison of Table VII with Table IV (Cu VII) and with Table V (Cu IX and Cu X) shows that the catalytic activity of reduced copper is not significantly affected by the addition of ethyl alcohol except that the catalyst (Cu XIV), prepared with potassium bicarbonate and used at the lower temperatures, is less active.

Catalysts. — Frolich et al.[3] reported that the gels precipitated at 85°C or higher temperatures consist essentially of copper oxide and only a small amount of copper hydroxide, and that lowering of the temperature of precipitation increases the amount of copper hydroxide. Further, it was found by Milligan[6] that the pure blue gel is hydrous cupric hydroxide and the black gel is hydrous cupric oxide. As shown in Table I, the precipitates obtained at various temperatures differ from each other in color. Thus the precipitates prepared at 5 and 22°C are blue, and these precipitates change gradually to dark gray in color. On the other hand, the precipitates prepared at 55 and 90°C are black. The precipitates resulting from lower precipitation temperatures are much more hydrated and bulky than those obtained at higher precipitation temperatures.

Orito and Kawachi[7] found that the activity of the mixed Cu-Cr basic carbonate catalyst for the liquid-phase hydrogenation of acetone is high when it is calcined previously at about 350°C and reduced before use in a stream of hydrogen. However, it seems that the copper prepared by direct reduction of basic copper carbonate possesses a higher dehydrogenation activity than that resulting from copper oxide.

Discussion

Cause of Condensation. — It was reported[8] that the copper catalyst, containing an alkaline oxide such as zinc oxide or magnesium oxide and composed of oxides having dehydrogenating and dehydrating properties, converts isopropyl

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6) W. O. Milligan, *J. Phys. & Colloid Chem.*, **55**, 497 (1951).

7) Y. Orito and S. Kawachi, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **60**, 703 (1957).

8) V. N. Ipatieff and V. Haensel, *J. Org. Chem.*, **7**, 189 (1942); L. L. Gershbein, H. Pines and V. N. Ipatieff, *J. Am. Chem. Soc.*, **69**, 2888 (1947); F. W. Major and F. E. Salt, Brit. Pat. 656405 (1951); *Chem. Abstr.*, **46**, 8147 (1952); S. Kudo, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **58**, 785 (1955). T. Kanamori, ibid., **61**, 1576 (1958).

alcohol to isobutyl methyl ketone and diisobutyl ketone along with others. As described in the preceding paper, similar condensation products were obtained by employing copper catalysts prepared with alkali hydroxides as precipitants. Such a condensation has not yet been reported to occur with a copper catalyst alone.

The present author first assumed that this condensation was caused by traces of alkali in the catalyst, but the copper catalyst prepared with an excess of potassium bicarbonate did not cause this condensation. Takayasu[9] determined the amounts of the residual oxide in various specimens of reduced copper, and observed that hydrogen might be incapable of reducing copper oxide completely into metallic copper. Further, he showed that the precipitates prepared by adding aqueous sodium hydroxide to aqueous copper nitrate at 100°C and at 30°C consist of $5CuO\cdot H_2O$ and $3CuO\cdot H_2O$, respectively. Audibert and Raineau[2] found that the precipitate prepared by adding an alkali hydroxide to a boiling solution of copper nitrate consists of $4CuO\cdot H_2O$. Ipatieff and Haensel[8] reported that an infinitesimal amount of water is required to start the condensation reaction. Considered from these items of information in the literature, the formation of the higher ketones in the present research seems also to be attributed to the effect either of traces of water or of a lower oxide of copper in the catalysts.

Summary

The present work is to determine whether the yields of acetone and of the oily products (isobutyl methyl ketone and diisobutyl ketone) to be obtained from isopropyl alcohol by the catalytic action of reduced copper are affected by the precipitation temperature in the preparation of the catalysts, and to find a catalyst efficient for the production of oily products. Isopropyl alcohol was changed to acetone in 91∼95% yield with no side reaction, by being passed over various copper catalysts at 325°C. The maximum yield of the oily products was obtained with the catalyst prepared with sodium hydroxide as a precipitant and at 22°C as the precipitation temperature, and at the reaction temperature of 220°C, amounting to 39.28% based on isopropyl alcohol used.

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[9] M. Takayasu, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaisi*), 64, 675 (1943), 65, 46 (1944).