

*Studies on Lactone Formation in Vapor Phase. I.
Synthesis of γ -Butyrolactone*

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Dehydrogenation of aliphatic glycols to the corresponding lactones with a copper catalyst was originated by Reppe^{1,2)} and later investigated by several investigators³⁻⁵⁾. The reaction was generally carried out in the following two ways: (1) Heating glycol and a small amount of copper chromite under continuous stirring at 200~250°C until hydrogen evolution ceased, (2) passing glycol with hydrogen over reduced copper supported on silica gel or pumice at the same temperature.

In Germany, γ -butyrolactone had been manufactured from 1,4-butanediol by the second method, and Copenhaver⁶⁾ has described its outline in "Acetylene and Carbon Monoxide

Chemistry". The yield of γ -butyrolactone (90%) was satisfactory but its space time yield was very small (about 0.015).

In order to find a more active catalyst for the vapor phase catalytic dehydrogenation of 1,4-butanediol to γ -butyrolactone, the activities of reduced copper supported on various carriers, the effects of the catalyst composition, and the reaction conditions have been examined.

Experimental

Catalyst.—The catalyst consisting of 20% copper and 80% zinc oxide was prepared as follows.

An aqueous solution 300 ml. containing 51 g. of cupric nitrate trihydrate was slowly added to 300 ml. of water in which 109 g. of zinc carbonate was suspended with stirring. Stirring was continued until the deposition of basic copper carbonate on zinc carbonate with evolution of carbon dioxide had ceased. The material was then washed three times with one liter of water, filtered and dried at 70°C. The final decomposition to copper oxide was carried out in a porcelain dish with frequent stirring and cautious heating at 300°C until the color of the

1) W. Reppe et al., Ger. Pat., 699945 (1940); *Chem. Abstr.*, **35**, 6977 (1941).

2) W. Reppe et al., *Ann.*, **596**, 158 (1955).

3) L. P. Kyrides and F. B. Zienty, *J. Am. Chem. Soc.*, **68**, 1385 (1946).

4) R. I. Longley et al., *ibid.*, **74**, 2012 (1952).

5) R. I. Longley et al., *Org. Synth.*, **35**, 87 (1955).

6) J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry", Reinhold Publishing Corp. (1949), p. 152.

TABLE I. EFFECTS OF CARRIERS ON YIELD

Carrier	B. D.* g.	Product g.	T. H. F.** g.	Yield of B. L.***		B. D. recovered g.	Conversion %
				g.	%		
AlO(OH)	24.8	19.5	3.0	9.0	45	1.8	93
SiO ₂	23.0	20.0	—	15.4	77	2.2	91
MgO	20.0	19.0	—	15.5	92	2.3	89
ZnO	23.4	22.0	—	20.9	95	0.4	98

* 1,4-Butanediol, ** Tetrahydrofuran, *** γ -Butyrolactone.

catalyst turned from light blue into dark brown.

When magnesium oxide was used as carrier, the catalyst was prepared similarly. In the case of alumina, copper hydroxide and aluminum hydroxide were coprecipitated with ammonia from the solution of copper nitrate and aluminum nitrate. In the case of silica gel, the catalyst was prepared from copper nitrate and sodium silicate by the usual manner. These catalysts were put in tablets, 8 mm. in diameter and 2 mm. in thickness. About 70 ml. of the tablets was used in each experiment.

Apparatus and Procedure.—The apparatus used is shown in Fig. 1. The dehydrogenation tube

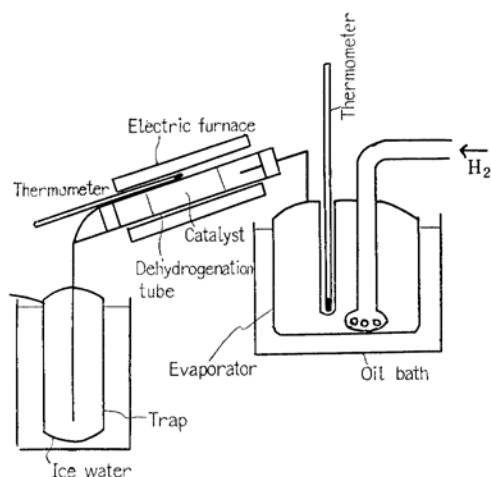


Fig. 1. Apparatus.

(60 cm. \times 15 mm.) was made from silica and heated in a furnace. Activation of the catalyst was carried out at 220°C in a stream of hydrogen until reduction was completed. The sample was passed in with a steady current of hydrogen. The evaporator containing 1,4-butanediol (n_D^{25} 1.4452, d_4^{25} 1.0130) was immersed in an oil bath and the feed speed of the sample was adjusted by regulating the temperature of the oil bath and rate of hydrogen. The evaporator was weighed before and after a run to determine the weight of material used. The reaction products were collected in a trap cooled by ice water, weighed and fractionated under a reduced pressure. γ -Butyrolactone (b. p. 98–100°C/25 mmHg) was easily fractionated from unreacted 1,4-butanediol (b. p. 142°C/25 mmHg). γ -Butyrolactone was a colorless liquid of n_D^{25} 1.4350, d_4^{25} 1.1264 and gave a hydrazide melting at 92°C.

Found: C, 40.92; H, 8.79. Calcd. for $C_4H_{10}O_2N_2$: C, 40.66; H, 8.53%.

Results and Discussion

Typical results for four carriers are tabulated in Table I.

The catalyst 70 ml. containing 20% copper was used. The reaction temperature was maintained at 230–240°C and the reaction time was one hour. The velocity of hydrogen passed with sample was 20 l. per hour. The yields of γ -butyrolactone were based upon the amount of butanediol consumed. With any carriers used, the conversion was very good. In the case of alumina, the yield was decreased owing to dehydration of butanediol to tetrahydrofuran. Magnesium oxide or zinc oxide was a superior carrier in respect to the yield

TABLE II. EFFECTS OF COPPER CONTENTS TO MAGNESIUM OXIDE

Cu-cont. %	B. D. used g.	Yield of B. L.		B. D. recovered g.	Con- version %
		g.	%		
10	25.5	20.6	96	3.0	88
20	20.0	15.5	92	2.3	89
30	23.0	19.4	95	1.6	93
40	25.0	22.0	94	0.5	98

TABLE III. EFFECTS OF COPPER CONTENTS TO ZINC OXIDE

Cu-cont. %	B. D. used g.	Yield of B. L.		B. D. recovered g.	Con- version %
		g.	%		
5	25.8	19.2	94	3.5	86
10	22.0	19.0	95	1.0	95
20	23.4	20.9	95	0.4	98
30	23.0	20.4	96	0.7	97
40	23.0	20.5	96	0.7	97

TABLE IV. EFFECTS OF THE REACTION TEMPERATURE

Reaction temp. °C	B. D. used g.	Yield of B. L.		B. D. recovered g.	Con- version %
		g.	%		
210	23.7	17.0	97	5.3	78
220	23.8	18.7	98	3.8	84
240	23.0	18.8	96	2.5	89
260	24.8	20.5	95	2.1	92
280	26.5	21.3	90	1.8	93
300	26.5	21.3	87	1.0	96
330	27.2	20.8	83	0.8	97

TABLE V. EFFECTS OF HYDROGEN VELOCITY AND LIQUID SPACE VELOCITY OF BUTANEDIOL

Velocity of H ₂ l./hr.	S. V.* of H ₂	Reaction time min.	B. D. used g.	L. S. V.** of B. D.	Yield of B. L.		S. T. Y.** of B. L.	B. D. recovered g.	Con- version %
					g.	%			
10	145	70	25.2	0.34	21.2	92	0.26	1.0	96
20	290	60	24.0	0.34	19.4	95	0.28	2.5	90
30	435	60	23.5	0.34	18.2	93	0.26	3.0	87
20	290	120	26.0	0.19	21.0	92	0.15	2.0	92
20	290	40	26.0	0.57	18.5	96	0.40	5.8	78
10	145	120	23.7	0.17	19.0	87	0.14	0.8	97
30	435	40	27.3	0.58	19.0	93	0.41	6.0	77

* Space velocity, ** Liquid space velocity, *** Space time yield.

and undesirable side reaction. These catalysts were prepared by the new method described in the experimental part.

Effects of the catalyst composition, relative ratio of copper to magnesium oxide and to zinc oxide, are shown in Tables II and III, respectively. The reaction conditions were the same as those in Table I. The suitable contents of copper were about 10~20%. The higher contents of copper did not improve the yield and conversion. Effects of the reaction temperature in the case of 20% copper-zinc oxide is shown in Table IV. The reaction time and the hydrogen velocity were the same as those of the above experiments. The conversion increased with the elevation of the reaction temperature and γ -butyrolactone was obtained in a good yield at 210~260°C. At above 280°C the product decreased owing to undesirable decompositions.

Finally, in use of the same catalyst as the above, effects of space velocity of hydrogen and liquid space velocity of butanediol on yield, space time yield and conversion were examined at 230~240°C and the results were summarized in Table V.

The yield was hardly affected with varying velocity of hydrogen and butanediol, but the

long contact with the catalyst lowered the yield to some extents. With increase of liquid space velocity from 0.17 to 0.58, the space time yield increased from 0.14 to 0.41, but the conversion decreased from 97% to 77%.

No final information was yet available as to the life of the catalyst, but its activity hardly decreased after several hours.

Summary

Vapor phase catalytic dehydrogenation of 1,4-butanediol to γ -butyrolactone with reduced copper supported on various carriers was studied. It was found that copper supported on zinc oxide or magnesium oxide was a superior catalyst. In the case of a catalyst consisting of 20% copper and 80% zinc oxide, the yield and space time yield of γ -butyrolactone were 95% and 0.28 at 230~240°C, respectively.

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