

Hydrogenation of Furfural and Furfuryl Alcohol. IV.

Hydrogenation of Furfural into Furfaryl (Tetrahydrofurfuryl) Alcohol by the Combination of Copper Chromium Oxide Catalyst and Nickel Kieselguhr Catalyst.

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This paper is the 7th report on the studies of furfural and its related compounds⁽¹⁾. In a previous report⁽²⁾, it was observed that the hydrogenation of furfural using nickel kieselguhr catalyst yields furfaryl alcohol or tetrahydrofurfuryl alcohol (about 60~75% of the theoretical yield), together with lower and higher boiling byproducts. On the other hand, the hydrogenation of furfural into furfuryl alcohol using copper chromium oxide catalyst⁽³⁾, and the hydrogenation of furfuryl alcohol into furfaryl alcohol using nickel kieselguhr catalyst⁽⁴⁾, proceed smoothly and furfaryl alcohol was obtained with little byproducts. It was suggested that for the production of furfaryl alcohol it seemed advantageous to carry out the hydrogenation in two steps, namely furfural into furfuryl alcohol using copper chromium oxide, and then furfuryl alcohol into furfaryl alcohol using nickel kieselguhr catalyst.

In this paper some investigations are reported on the hydrogenation of furfural into furfaryl alcohol by using both copper chromium oxide catalyst and nickel kieselguhr catalyst.

Furfural (1 mol) was hydrogenated into furfuryl alcohol by using copper chromium oxide catalyst at about 140°C, absorbing about 1 mol of hydrogen. This reaction product was then hydrogenated by adding nickel kieselguhr catalyst, without separation and purification of furfuryl alcohol. About 2 mol hydrogen was absorbed rapidly at about 120°C, and then furfaryl alcohol (yield about 83-84% of the theoretical), was obtained with little byproducts (see experiments P 51 and P 68 in the Table 1).

In the previous report it was observed and concluded that furfural was intrinsically more inert than furfuryl alcohol against the hydrogenation over nickel kieselguhr catalyst, but it was not due to the presence of a small amount of catalyst poison, like thiophene in benzene. The present experimental results that the hydrogenation of the second step proceeds

(1) M. Katuno: *Soc. Chem. Ind., Japan*, **46** (1943), 25 B, 180 B, 184 B, 210 B, 214 B.

(2) M. Katuno: *ibid.*, **46** (1943), 25 B.

(3) M. Katuno: *ibid.*, **46** (1943), 180 B.

(4) M. Katuno: *ibid.*, **46** (1943), 184 B.

rapidly, also confirm that furfural does not contain catalyst poison, such as sulphur compounds.

Furfural (1 mol) was then hydrogenated at about 140°C, by using copper chromium oxide catalyst and nickel kieselguhr catalyst together, which were prepared separately before use by thermal decomposition of $\text{Cu(OH)(NH}_4\text{)(CrO}_4\text{)}$ and by reduction of NiCO_3 -kieselguhr. About 3 mol of hydrogen were absorbed, and furfuryl alcohol (about 74-79% of theoretical yield) was separated from the product. The yield was slightly lower than in the above-mentioned method, and small amounts of byproducts were observed (P 52 and P 61). In this hydrogenation, it is probable that furfural is partly hydrogenated in two steps, first into furfuryl alcohol by copper chromium oxide catalyst, and then into furfuryl alcohol by nickel catalyst, in good theoretical yield, and partly hydrogenated directly into furfuryl alcohol by the nickel catalyst with considerable amounts of lower and higher boiling byproducts, as observed in the previous reports⁽⁵⁾. The yields are, therefore, a little lower than in the above two step hydrogenation.

In the above experiments, copper chromium oxide catalyst and nickel kieselguhr catalyst were prepared separately before use from $\text{Cu(OH)(NH}_4\text{)(CrO}_4\text{)}$ and Nickelcarbonate-kieselguhr, respectively. Mixed catalysts of $\text{Cu(OH)(NH}_4\text{)(CrO}_4\text{)}$ and NiCO_3 -kieselguhr were then employed for the hydrogenation of furfural. Both catalysts were mixed mechanically by grinding in a mortar in the ratio of 1:1 or 1:2 by weight, or mixed in the state of precipitates as described in the experimental details.

Furfural (1 mol) was hydrogenated at about 140°C by using the mechanically mixed catalyst, which was reduced at about 250°C, before use (Expt. P 53). About 1 mol of hydrogen was absorbed rapidly and then hydrogenation became slow, and about 1.33 mol of hydrogen was absorbed in about $4\frac{25}{60}$ hrs. The absorption of hydrogen is also slow by the rise of the temperature to about 160°C after hydrogenation at about 140°C (Expt. P 107). These results show that nickel is not reduced inductively by copper, probably because of the unintimate contact between nickel and copper. By the reduction at about 400°C after reduction at about 250°C, the catalyst can hydrogenate furfural into furfuryl alcohol in about 70% theoretical yield, absorbing about 3 mols of hydrogen, owing to the reduction of nickel (Expt. P 62).

The mixed catalyst in the state of precipitation, after reducing at about 250°C, can hydrogenate furfural into furfuryl alcohol, absorbing about 3 mols of hydrogen, owing to the induced reduction of nickel (Expt. P 72). The catalyst, after thermal decomposition at about 250°C without reduction, cannot hydrogenate furfural into furfuryl alcohol,

(5) M. Katuno: *J. Soc. Chem. Ind., Japan*, **46** (1943), 25 B.

the hydrogenation becoming slow after rapid absorption of about 1 mol of hydrogen, and about 1.26 mol of hydrogen was absorbed in about $5\frac{15}{60}$ hrs. (Expt. P 106').

These results using mixed catalysts are inferior to the above results using two catalysts prepared separately before use.

Experimental Details. 1. *Catalysts: Copper chromium oxide catalyst:* It was prepared as described in the previous report⁽⁶⁾, following the description of Edgar and Calingaert⁽⁷⁾ with slight modification. Namely, brown precipitate $\text{Cu}(\text{OH})(\text{NH}_4)(\text{CrO}_4)$ was prepared from copper nitrate and ammonium bichromate solution with ammonia water, washed with water, filtered, dried in a steam oven and powdered and stored in a desiccator. It was decomposed into $2\text{CuO} + \text{Cr}_2\text{O}_3$ by heating at about 250°C for one hour.

I:I (by weight)-nickel-kieselguhr catalyst: It was prepared as described in the previous report⁽⁸⁾. Nickel carbonate was precipitated on kieselguhr in the ratio $\text{Ni}:\text{kieselguhr} = \text{I}:\text{I}$ (by weight), from Nickel nitrate solution with sodium carbonate and a small amount of sodium hydroxide. The precipitate was washed, filtered, dried in a steam oven, powdered and stored in a desiccator. It was reduced at about 450°C in a stream of hydrogen for one hour before use. *Mechanically mixed catalyst of copper chromium oxide and nickel kieselguhr catalyst:* $\text{Cu}(\text{OH})(\text{NH}_4)(\text{CrO}_4)$ and nickelcarbonate-kieselguhr were mixed in the ratio of $\text{I}:\text{I}$ and $\text{I}:\text{2}$ by weight by grinding in a mortar. For the reduction of the catalyst, it was heated to about 250°C in a stream of carbon dioxide gas and then hydrogen was introduced very slowly at first and finally rapidly⁽⁹⁾, in order to prevent the temperature rise of the catalyst.

Mixed catalyst of copper chromium oxide and nickel kieselguhr in the state of precipitates: $\text{Cu}(\text{OH})(\text{NH}_4)(\text{CrO}_4)$ was precipitated from calculated amounts of copper nitrate solution (content of copper was analysed) and (ammonium bichromate with ammonia water, which was neutralised with nitric acid solution when added in excess, in order to precipitate copper as completely as possible. The precipitate of $\text{Cu}(\text{OH})(\text{NH}_4)(\text{CrO}_4)$ was washed by decantation. On the other hand, a calculated amount of nickel carbonate was precipitated on kieselguhr (nickel: kieselgur = $\text{I}:\text{I}$ by weight) from calculated amount of nickel nitrate solution (content of Ni was analysed) with sodium carbonate and a small amount of sodium hydroxide solution, and the precipitate was

(6) M. Katuno: *J. Soc. Chem. Ind., Japan*, **46** (1943), 180 B.

(7) G. Edgar & G. Calingaert: *Ind., Eng. Chem.* **26** (1934), 878.

(8) M. Katuno: *J. Soc. Chem. Ind., Japan*, **46** (1943), 25 B.

(9) M. Katuno: *J. Soc. Chem. Ind., Japan*, **45** (1942), 390 B.

washed. The two precipitates were then mixed together intimately, filtered, dried, powdered and stored in a desiccator. The amount of copper and nickel were calculated for $\text{Cu}(\text{OH})(\text{NH}_4)(\text{CrO}_4)$: nickelcarbonate-kieselguhr = 1:1 by weight. The reduction of the catalyst was carried out as described before.

2. *Hydrogenation*: A horizontal shaking autoclave of about 660 cc. content was used. The hydrogenation was carried out with the initial pressure of about 88–102 atm; (at room temperature). Hydrogen was charged from bomb when the pressure dropped below 50 atm. Hydrogenation was continued in the most cases till the pressure became constant after complete hydrogenation. Furfural used was redistilled under reduced pressure and had yellow or light brown color.

3. *Fractionation of the products*: The procedure is the same as that in the previous paper⁽¹⁰⁾. The product was pipetted out into 300 cc. modified Claisen flask⁽¹¹⁾ or three necked flask⁽¹¹⁾, and weighed. The product was fractionated using 20 cm. Widmer column, first under atmospheric pressure, and the fraction boiling up to 90°C was separated (Fraction A), which consists mainly of the aqueous azeotropic mixture of methyltetrahydrofuran, etc. in the case of the hydrogenation using nickel catalyst. The pressure was then reduced to about 50–90 mm., and the fraction boiling up to 80–90°C was collected (Fraction B). This fraction consists of a considerable amount of water, and probably, the aqueous azeotropic mixture of n-amyl alcohol mainly.

The pressure was then reduced to about 20 mm., and the fraction boiling up to 90°C was collected (Fraction C). This fraction boils constantly at about 80°C under 20 mm., and consists mainly of furfuryl alcohol in the case of nickel catalyst, and mainly of furfuryl alcohol in the case of incomplete hydrogenation (Expt. P 53, P 106, P 107). In some cases the liquid in the flask was distilled at the temperature below 90°C. The fraction C was regarded as crude furfuryl alcohol or, in a few cases (P 53, P 106, P 107), as furfuryl alcohol.

The distillation was further continued till the decomposition took place, and the distillate (fraction D) probably consists of pentanediols. The residue (fraction E) consists of the catalyst and the more highboiling viscous substance.

Summary.

1. Furfural was hydrogenated into furfuryl alcohol by using copper chromium oxide catalyst under high pressure. Then the product was

(10) M. Katuno: *J. Soc. Chem. Ind., Japan*, **46** (1943), 25 B.

(11) M. Katuno: *J. Soc. Chem. Ind., Japan*, **46** (1943), 209 B.

further hydrogenated by adding nickel kieselguhr catalyst, without separation and purification of furfuryl alcohol. The hydrogenation proceeded rapidly and furfuryl alcohol about 83-84% of the theoretical yield was obtained.

2. Furfural was hydrogenated by using copper chromium oxide catalyst and nickel kieselguhr catalyst, which were prepared separately before use. The hydrogenation proceeded rapidly, and furfuryl alcohol, (about 74~79% of the theoretical yield) was obtained, which is slightly lower than in the above procedure.

3. The mixture of $\text{Cu}(\text{OH})(\text{NH}_4)(\text{CrO}_4)$ and nickel carbonate kieselguhr, mixed mechanically or in the state of precipitates, was used for the hydrogenation of furfural, after reducing it with hydrogen or after thermal decomposition without reduction. The results was less satisfactory compared with the above two procedures.

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Table 1. Hydrogenation of furfural (96 g. or 1.0 mol of furfural was used.)

Exptl. No.	Catalyst	Hydrogenation				Fractionation of the product					References			
		Amount of Cu or Ni (g)	Temp. (°C)	Time drop (hrs)	Pressure (atm)	Absorption of H ₂ (mol)	Fract. C (crude furfuryl alcohol)							
							Fract. A (g)	Fract. B (g)	Yield (mol)	Theor. yield (%)		Fract. D (g)	Residue (g)	
P 61	2CuO + Cr ₂ O ₃ followed by 1:1-Ni-kieselguhr	1.2 2.6	(137-146°) (117-121°)	3 ²⁵ ₆₀ 2 ⁵⁵ ₆₀	43.1 78.6	1.07 1.93	0 1.1	85.2	0.885	83.5	0	15.0		
P 68	2CuO + Cr ₂ O ₃ followed by 1:1-Ni-kieselguhr	1.2 1.3	(138-143°) (116-124°)	4.0 2 ⁴⁰ ₆₀	42.7 84.2	1.05 2.06	0 1.4	85.0	0.832	83.2	0	8.3		
P 52	2CuO + Cr ₂ O ₃ 1:1-Ni-kieselguhr (Prepared separately and used together.)	1.2 2.6	(138-139°) (140°)	3 ⁵⁵ ₆₀ 3 ⁵⁵ ₆₀	126.9 125.9	3.11 3.08	67-90° 0-5	86°/86-88°/86 80.3	0.787	78.7	—	20.7		
P 61	2CuO + Cr ₂ O ₃ 1:1-Ni-kieselguhr (Prepared separately and used together.)	1.2 1.3	(138-144°) (140°)	3 ⁵⁰ ₆₀ 3 ⁵⁰ ₆₀	129.7	3.18	0 0.2	67°/74-80°/74 75.9	0.743	74.3	100°/20-100°/10	19.1		
P 106	2CuO + Cr ₂ O ₃ 1:1-Ni-kieselguhr	1.2 1.3	(138-144°) (138-135°)	3.0 1 ⁵⁵ ₆₀	45.8 0.0	1.12 0.00	— 5.9	88°/82-85°/82 (52.7) ⁽³⁾	(0.538) ⁽³⁾	(53.8) ⁽³⁾	88°/18-125°/18	31.5	Resinification took place a little.	
P 53	2CuO + Cr ₂ O ₃ 1:1-Ni-kieselguhr (Mixed catalyst ⁽²⁾ by precipitation was heated at 250° for 1 hr.)	1.2 2.6	(137-145°) (140°)	4 ²⁵ ₆₀ 4 ²⁵ ₆₀	54.0	1.33	70-90° 0.6	47°/76-72°/76 (85.5) ⁽³⁾	(0.872) ⁽³⁾	(87.2) ⁽³⁾	0	14.5		
P 107	2CuO + Cr ₂ O ₃ 1:1-Ni-kieselguhr	1.2 1.3	(138-145°) (138-135°)	1 ¹⁵ ₆₀ 2 ³⁵ ₆₀	46.3 11.1	1.14 0.27	— 4.3	88°/80-80°/85 (62.5) ⁽³⁾	(0.637) ⁽³⁾	(63.7) ⁽³⁾	88°/22-125°/25	28.0	Resinification took place a little.	
P 62	2CuO + Cr ₂ O ₃ 1:1-Ni-kieselguhr (Mechanically mixed catalyst ⁽²⁾ was reduced at 250° for 1 hr.)	1.2 1.3	(138-142°) (138-161°)	5 ⁵ ₆₀ 2 ²⁵ ₆₀	93.6 11.9	2.30 0.29	0 2.4	47°/88-100°/82 71.2	72°/102°/22	0.698	69.8	100°/22-100°/22	22.6	
P 72	2CuO + Cr ₂ O ₃ 1:1-Ni-kieselguhr (Mechanically mixed catalyst ⁽²⁾ was reduced at 250° then at 400° each for 1 hr.)	1.2 1.3	(138-140°) (138-161°)	2 ¹⁰ ₆₀ 3 ¹⁵ ₆₀	50.5 74.9	1.24 1.84	71-80° 0.4	47°/88-100°/85 67.7	80°/21-96°/22	0.663	66.3	88°/22-124°/22	27.6	
(Mixed catalyst ⁽²⁾ by precipitation was reduced at 250° for 1 hr.)		Total			127.8	3.14								

(1) Calculated assuming the volume of gas in the autoclave to be about 550 cc., and the gas to be a perfect gas.
 (2) Mixture of Cu(OH)(NH₄)(CrO₄) and Nickelcarbonate-kieselguhr (Nickel:kieselguhr=1:1).
 (3) Regarded and calculated as crude furfuryl alcohol.