

[CONTRIBUTION FROM THE JOHN STUART RESEARCH LABORATORIES OF THE QUAKER OATS COMPANY]

Catalytic Hydrogenation. I. Kinetics and Catalyst Composition in the Preparation of 2-Methylfuran

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The rates of formation of 2-methylfuran and by-products from the vapor phase hydrogenolysis of furfuryl alcohol are reported. 2-Pentanol and 2-methyltetrahydrofuran are formed by further reaction of 2-methylfuran, while some tetrahydrofurfuryl alcohol is formed by a competing reaction. The kinetics indicate that 2-methylfuran may be prepared in substantially quantitative yields over a copper chromite catalyst.

Investigation of the liquid-phase hydrogenolysis of furfural to 2-methylfuran over various copper and copper chromite catalysts has given occasional yields as high as 90% at temperatures ranging from 200° to 290°.¹ Somewhat better results have been reported in vapor phase reactions. Bremner *et al.*^{2,3} have reported 85–90% yields from furfural at 200–300°C. Lukes and Wilson^{3a} report at best an 80% yield over a copper-iron catalyst under similar conditions. Others^{4,5} report similar results around 200° from furfural using an Adkins type copper chromite, but only a 70% yield when furfuryl alcohol was used as a starting material. These results are not in agreement with the present results in which an 88% yield was obtained when furfural was used as the liquid feed and 95% or better using furfuryl alcohol.

The function of calcium or barium oxides in copper chromite catalysts (Adkins type) is generally considered to be that of a selective promotor in hydrogenation reactions. Since in the present work (Table I), no significant difference was observed in yields or in rates of reaction over catalysts which contained the alkaline earth metal oxides, as compared with those which did not, it must be concluded that these oxides have no apparent effect on the type of hydrogenolysis reaction under discussion.

The addition of a small amount of sodium silicate to copper chromite resulted in very poor yields at temperatures up to 300° as shown in Table I and the resulting catalyst behaved more like copper than copper chromite. This effect can be attributed to either a reaction with the active copper chromite catalyst which would decrease its acidity in a Lewis sense, or a physical distortion of the lattice acting then as a lattice defect poison. In any event, it confirms the effect noted by Brem-

ner and Keeys³ that basic additives decrease catalyst activity from the standpoint of hydrogenolysis.

A copper catalyst, contrary to results reported⁶ earlier, gave poor yields of methylfuran and acted primarily as a hydrogenation catalyst with very little tendency toward hydrogenolysis. Apparently at temperatures above 250°, this catalyst has little effect on the rate of formation of methylfuran.

Although any of the catalysts employed may be used without prior reduction, the catalyst actually becomes reduced during the reaction period. This process, which is highly exothermic for copper chromite catalysts, results in uncontrollable hot zones in the catalyst bed causing poor yields of methylfuran. Reduction of the catalysts at temperatures below 250° with controlled mixtures of hydrogen and nitrogen permits a smooth reaction and gives a catalyst of better activity and life than those not previously reduced. Catalysts which were reduced at temperatures of 300° or higher were less active than those reduced below 250° since they required temperatures about 30° higher to give similar conversions and yields. This temperature effect is presumably due to distortion of the physical structure of the catalyst resulting in fewer undisturbed positions for the adsorption of hydrogen or furfuryl alcohol.

Of the three copper chromite catalysts (No. 1, 2, 3) containing only copper chromite which were investigated, the best conversions were obtained on that which contained 80% copper oxide prior to reduction. The active catalyst is reported⁷ to be $\text{Cu}_2\text{Cr}_2\text{O}_4 + \text{Cu}$ which would be approximately 60% copper oxide before reduction. There is little difference between catalysts 1 and 2 except in conversion at the lower temperatures. These two catalysts bracket the desired 60% and would be expected to be similar. The reasons for the lower conversions observed with catalyst 1 are not understood at the present time, but the results appear to indicate that excess chromium oxide has a detrimental effect.

(1) See for example K. Tsuda *et al.*, *Chem. Abstr.*, **45**, 6182 (1951). M. Okawara, *Chem. Abstr.*, **47**, 4832 (1953).

(2) J. Bremner, R. Keeys, and D. Jones, *Brit. Patent 634,079* (1947).

(3) J. Bremner and R. Keeys, *J. Chem. Soc.*, 1068 (1947).

(3a) R. Lukes and C. Wilson, *J. Am. Chem. Soc.*, **73**, 4790 (1951).

(4) R. F. Holdren, U. S. Patent **2,445,714** (1948).

(5) L. W. Burnett, Ph.D. thesis, Iowa State College, 1943.

(6) H. Guinot, U. S. Patent **2,456,187** and French Patent **973,322**.

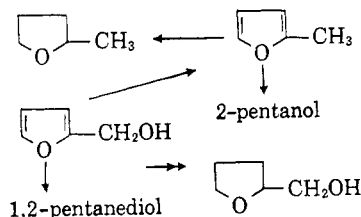
(7) J. D. Stroupe, *J. Am. Chem. Soc.*, **71**, 569 (1949).

TABLE I

Catalyst No.	Composition ^a (%)	T (°C.)	MeF (%) ^b	MeTHF (%)	2-Pentanol (%)	THFA (%)	FA (%)	Diol (%)
1	52 CuO	200	92.1	3.7	1.5	0.5	0.1	2.1
	36 Cr ₂ O ₃	175	33.3	—	0.2	0.1	65.3	1.1
		150	8.6	0.7	—	—	90.5	0.2
2	80 CuO	200	92.2	1.8	1.8	1.7	—	2.5
	17 Cr ₂ O ₃	175	70.8	1.6	0.8	0.2	23.6	2.0
	2 Graphite	150	25.4	0.4	0.5	—	72.7	1.0
3	94 CuO	200	83.8	3.2	5.7	1.0	2.1	4.2
	6 Cr ₂ O ₃	175	66.4	1.2	4.5	0.1	23.4	4.4
		150	16.7	0.5	0.4	—	81.2	1.2
4	46 CuO	200	93.1	3.6	1.7	1.0	0.2	0.4
	50 Cr ₂ O ₃	175	87.9	2.1	0.6	0.2	8.5	0.7
	4 CaO	150	17.7	0.8	0.4	0.1	80.7	0.3
5	72 CuO	300	44.8	11.5	4.6	2.1	35.1	1.9
	15 Cr ₂ O ₃	275	41.8	10.1	4.9	1.0	39.6	2.6
	12 Na ₂ SiO ₃	250	32.8	4.0	3.1	1.4	55.6	3.1
6	96 CuO	300	2.8	0.5	0.2	—	96.0 ^c	0.5
	4 Graphite	250	4.1	14.8	0.6	—	78.0 ^c	2.5
		200	1.2	2.9	0.2	—	95.0 ^c	0.7

^a Non-reduced tablets, prepared and analyzed by The Harshaw Chemical Co., Catalyst Div. ^b For method of analysis see experimental section. MeF = 2-methylfuran, MeTHF = methyltetrahydrofuran, THFA = tetrahydrofurfuryl alcohol, diol = 1,2-pentanediol, FA = furfuryl alcohol. ^c Qualitative analysis indicates that this is largely FA in agreement with the results of Bremner and Keays.³

On the basis of the products observed and the data obtained, the reaction sequence involved must be as shown



The 1,2-pentanediol must be a product of direct reaction of furfuryl alcohol since tetrahydrofurfuryl alcohol did not form this product under these conditions. Also 2-methyltetrahydrofuran and 2-pentanol are formed by further reaction of 2-methylfuran since neither of these products are formed from tetrahydrofurfuryl alcohol in yields of greater than 1%. This conclusion is also drawn from the results shown in Table II where the yield of pentanol is reported under similar conditions of feed rate and gas flow. Traces of 2-pentanone were found occasionally, in contrast to the reported⁸ results which were obtained at very low gas to feed ratio.

TABLE II

CONVERSION TO PENTANOLS OVER CATALYST 2

MeTHF feed		MeF feed	
T (°C.)	% Conversion	T (°C.)	% Conversion
200	<2	120	3
300	9	150	21
400	35	180	63

(8) C. Wilson, *J. Am. Chem. Soc.*, **70**, 1313 (1948).

The rate of formation of 2-methylfuran (hydrogenolysis of side chain) is increased more rapidly by a temperature increase than either the rate of formation of tetrahydrofurfuryl alcohol (hydrogenation of nucleus) or pentanediol (hydrogenolysis of the nucleus). From the kinetic data, there is a temperature at which the conversion of furfuryl alcohol to 2-methylfuran reaches a maximum. Any further increase in temperature serves mainly to increase the rate of formation of other products. The actual temperature would be expected to depend on rate of feed as well as contact time. However, Table III shows that the rate of hydrogen flow had essentially no effect on the composition of the product in the range of 8:1 to 30:1 mole ratio of hydrogen to feed. A rather significant decrease in the amount of hydrogenolysis products (pentanediol and pentanol) was observed when the rate of feed was increased, while no such change was observed in the amounts of hydrogenated products. Since it was previously established that copper acts primarily as a hydrogenation catalyst, it may be concluded that the hydrogenation reactions must require an active site on a portion of the catalyst which is copper whereas the hydrogenolysis requires copper chromite.

TABLE III

Effect of gas flow and feed rate at 218°C. over catalyst 2

Feed rate	20 g./hr.	20 g./hr.	5 g./hr.
Gas flow	30:1	10:1	10:1
MeF	91.5	93.1	84.8
MeTHF	3.2	3.4	4.0
2-Pentanol	1.5	0.8	2.1
THFA	1.4	0.4	0.8
1,2-Pentanediol	2.5	2.3	8.3

Since the three hydrogenolysis reactions are competing, with the formation of 2-methylfuran being the lower energy process, an increase in feed rate leads to the preferential formation of 2-methylfuran. A saturation point would probably be reached where the formation of pentanol would not occur and the formation of pentanediol would be minimized.

In the calculation of kinetic data, the rate constants were taken as percentage yields. For 2-methylfuran the rate constants, shown in Table IV, were taken as the yield of 2-methylfuran plus the yields of 2-methyltetrahydrofuran and pentanol in keeping with the assumption that these products arise from further reaction of methylfuran. Further evidence for this assumption was obtained by taking samples at various depths in the catalyst bed. When about half of the catalyst bed length was used the yield of methylfuran was 99%. A plot of $-\log k$ vs.

3.0 for catalyst 1, 35.7 ± 3.0 for catalyst 2, 38.7 ± 3.0 for catalyst 3, and 28.7 ± 3.0 for catalyst 4.

EXPERIMENTAL

Apparatus. The reaction chamber was a vertical glass tube 20 in. long and 20 mm. in diameter, externally heated by means of nichrome wire, containing 2 thermocouples at 6 and 12 in. depths, and a glass wool plug as support for the catalyst. A glass vaporizer was constructed to permit admixture of the preheated hydrogen and feed before entering the reaction chamber. The product was cooled by means of a cold water condenser followed by dry ice traps. The hydrogen gas was vented to the atmosphere after the cooling traps.

Typical run. A catalyst charge of 160 g. was used. The catalyst was reduced by heating to 140° under a nitrogen flow of 413 liters/hr. and a hydrogen flow of 45 liters/hr. The nitrogen flow was gradually cut to zero over 3 hr. and the temperature was then raised to 210° until no further evolution of water of reduction occurred. The water given off from catalyst 2 corresponded to a reduction of 71% of the catalyst. When the reduction reached this point, the hydrogen flow was raised to 63 l./hr. and furfuryl alcohol (Q.O. FA) was added to the vaporizer by means of a peristaltic action pump at a rate of 20 g./hr. At least a 1 hr. conditioning run was used in all cases and the actual run was made over a period of 3 to 4 hr. In all runs used for the kinetic data, this feed rate and gas flow were used.

Catalysts. All catalysts used were prepared and analyzed by The Harshaw Chemical Company and were one-eighth inch tablets.

Analysis of products. The organic layer was analyzed using a Perkin-Elmer Vapor Fractometer containing a column packed with material in which didecyl phthalate was the stationary liquid phase. Analysis of the water layer showed not more than 0.2% of any one component and was not used in the calculations. To arrive at an analysis of the product for furfuryl alcohol, the product was distilled up to 101° and the residue was analyzed by the Hughes-Acree technique.

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TABLE IV
LOGARITHM OF RATE CONSTANTS FOR FORMATION OF MEF

Catalyst	200°	175°	150°	125°	100°
1	1.984	1.525	0.973	—	—
2	1.982	1.874	1.420	0.204	-0.689
3	1.967	1.858	1.248	0.431	—
4	1.986	1.988	1.093	0.380	+0.041

$1/T$ did not show any differences in slope for each copper chromite catalyst which could not be attributed to experimental error. Therefore the values were averaged and plotted to obtain 24.1 ± 1.8 k cal/mole for the heat of activation in the formation of methylfuran. Similar calculations for the formation of tetrahydrofurfuryl alcohol gave increasing heats of activation as the copper content of the catalyst increased. The figures are $26.7 \pm$