Studies on Acetylene and its Derivatives. (IX)

The Catalytic Conversion of Acetaldehyde to Acetone. (4). On Reaction Conditions[1]

Toshizo ISOSHIMA*

(Nodzu Laboratory)

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This paper presents the optimum reaction conditions in the synthesis of acetone from acetaldehyde and water in vapor phase.

ZnO or Fe_2O_3 was proved to be the best catalyst, followed by CdO or PbO. The optimum reaction conditions were found to be as follows :

(1) the concentration of acetaldehyde in the aqueous solution lower than 3g. CH_3CHO/10 cc. aq. solution ;

(2) the reaction temperature, 400-450°C ;

(3) the rate of dropping of the aqueous solution of acetaldehyde, 10 cc./hr.

INTRODUCTION

In the third paper[2] of this series, attention has been drawn to the research of good catalysts in the synthesis of acetone from acetaldehyde and water in vapor phase.

$$2CH_3CHO + H_2O \longrightarrow CH_3COCH_3 + 2H_2 + CO_2 \quad (I)$$

The present investigation was undertaken to determine the optimum reactions. With the catalyst of ZnO, CdO, PbO, Fe_2O_3, CaO, or MnO_2, the effect of reaction temperature has been investigated. With ZnO, Fe_2O_3, or CaO, the effect of the concentration of acetaldehyde has been studied with ZnO, the optimum rate of dropping has been determined. In this investigation ethyl acetate and ethyl alcohol in the produced liquid were also analyzed besides acetic acid, acetaldehyde, and acetone to study the reaction mechanism of the formation of acetone.

EXPERIMENTAL

(1) **Apparatus**, (2) **Procedure**, and (3) **Methods of preparation of catalysts** were the same as those described in the third paper of this series.[2]

(4) **Reaction Conditions** : Catalyst, 30 cc. ; Length of catalyst bed, 30 cm ; Reaction temperature, 300-500°C ; Volume of the aqueous solution of acetaldehyde, 25 cc ; Rate of dropping of the aqueous solution of acetaldehyde, 5-20 cc./hr.

(5) **Analysis of reaction products**

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* 磯島敏三

(a) Analysis of produced liquid : The produced liquid was diluted to 500 cc. with water, and then acetic acid, acetaldehyde, acetone, ethyl acetate and ethyl alcohol were determined according to the methods described in the second paper of this series.[3]

(c) Gas analysis : The gases (CO_2, C_nH_{2n}, O_2, CO, H_2, CH_4, N_2) formed were analyzed by Hempel's and combustion method.

RESULTS

1. Effect of Reaction Temperature. In Table 1 is shown the effect of reaction temperature (300-500°C) upon the converion ratio of acetaldehyde and the yield of acetone. From these data, actions of catalysts are considered.

No catalyst : At 300-500°C, no acetone was produced. On the other hand, the decomposition of acetaldehyde seems to predominate, for the formed gas was mostly composed of CO and CH_4.

ZnO : At 450°C, the conversion ratio was 98% and the yield of acetone was the maximum of 79%. The ratio of H_2 to CO_2 in the formed gas was about 2, so the normal reaction (formula (I)) of acetone formation seems to occur mainly.

Fe_2O_3 : The conversion ratio was more than 95% above 400°C, and the yield of acetone was the maximum of 80% at 400°C. The ratio of H_2 to CO_2 was 1.45-1.90.

CaO : The yield of acetone was very low below 300°C, but began to increase from 400°C and reached the maximum of 46% at 450°C. Since the decomposition temperature of calcium acetate, which is considered as an intermediate to acetone formation, is above 420°C, those results seem to be probable. The yield of ethyl alcohol was 25% at 400°C and higher than with other catalysts. The formed gas contained solely H_2 and no CO_2, for CO_2 had been fixed on catalyst as calcium carbonate (decomposition temperature is 825°C).

CdO : With the rise of the reaction temperature, the conversion ratio increased, and the yield of acetone was the maximum of 69% at 400°C. It seems due to the reduction of CdO that the ratio of H_2 to CO_2 was far smaller than 2.

PbO : The yield of acetone was the maximum of 75% at 450°C. The ratio of H_2 to CO_2 was too small, essentially the same as with CdO.

MnO_2 : The conversion ratio was 96% at 450°C, and the yield was the maximum of 23% at 400°C.

From these obtained results, it was found that ZnO or Fe_2O_3 is the best catalyst and the optimum reaction temperature is 500°C.

2. Effect of Concentration of Acetaldehyde in the Aqueous Solution. The data given in Table 2 show the effect of concentration of acetaldehyde in the aqueous solution.

(i) Effect of high concentration of acetaldehyde. With the catalyst of ZnO,

Table 1. Effect of Reaction Temperature.

(Catalyst 30 cc. ; 30 % Aq. Solution of CH_3CHO 25 cc. ; Rate of Dropping of Aq. Solution of CH_3CHO 10 cc./hr.)

Catalyst	Aq. Soln. of CH_3CHO		React. Temp. (°C)	Conv. ratio of CH_3CHO (%)	Products				Yield of CH_3COCH_3 (%)	Gas Analysis (%)					H_2/CO_2
	CH_3CHO (g)	CH_3COOH (g)			CH_3COOH (g)	CH_3COCH_3 (g)	CH_3COOEt (g)	EtOH (g)		CO_2	C_nH_{2n}	CO	H_2	CH_4	
None	7.313	0.214	300	13.3	0.813	0	—	—	0	—	—	—	—	—	—
〃	7.973	0.225	400	17.9	0.577	0	—	—	0	3.0	0	46.5	2.0	48.5	—
〃	7.950	0.090	500	26.0	0.357	0	—	—	0	4.3	0.4	51.6	0	43.7	—
ZnO	6.948	0.052	300	37.0	0.264	0.134	—	—	7.8	33.2	0	0.2	66.6	0	2.00
〃	7.643	0.039	350	72.5	0.053	1.213	0.380	0.540	34.2	30.2	1.2	1.4	65.2	2.0	2.16
〃	6.498	0.196	400	87.8	0.067	2.786	0.400	0.140	74.0	33.0	0.9	1.6	64.5	0	1.96
〃	6.740	0.089	450	98.0	0	3.467	0.170	0.792	79.6	31.1	1.1	1.1	62.7	4.0	2.01
〃	6.635	0.098	500	91.7	0.022	2.703	0.204	0.196	67.4	30.0	1.4	1.1	65.0	2.5	2.17
Fe_2O_3	6.138	0.099	300	45.4	0.020	0.129	0.473	0.252	7.0	35.8	2.1	3.2	58.9	0	1.65
〃	7.520	0.021	350	63.0	0.300	1.860	0.809	0.460	56.4	34.9	0.6	6.5	50.7	7.3	1.45
〃	6.463	0.258	400	95.7	0.168	3.280	—	—	80.3	36.8	1.3	0.3	61.6	0	1.67
〃	7.035	0.370	425	99.2	0	3.689	0.210	0.655	80.2	37.3	1.2	0.7	59.1	1.7	1.58
〃	6.668	0.076	450	94.6	0.055	3.041	0.323	0.541	73.2	36.1	1.0	5.1	52.4	5.4	1.45
〃	7.103	0.097	500	98.9	0.025	3.222	0.380	0.356	69.6	32.4	0.6	2.6	61.7	2.7	1.90
CaO	6.995	0.200	250	51.9	0.200	0	0.606	0.576	0	—	—	—	—	—	—
〃	6.818	0.211	300	51.5	0	0.039	0.687	0.387	1.7	—	—	—	—	—	—
〃	7.618	0.112	400	54.9	0	0.813	0.404	1.111	29.5	0	0	6.6	93.4	0	—
〃	7.005	0.253	450	83.1	0	1.774	0.259	0.670	46.2	2.1	1.1	1.4	91.2	4.2	—
〃	6.795	0.062	500	94.7	0	1.746	0.178	0.842	41.1	2.0	1.0	4.9	88.0	4.1	—
CdO	7.863	0.123	400	77.6	0.350	2.806	—	—	69.6	46.0	4.5	1.8	43.2	4.5	0.94
〃	7.753	0.025	450	85.9	0.251	2.907	0.458	0.037	66.2	57.7	5.0	4.5	30.1	2.7	0.52
〃	8.180	0.086	500	81.1	0.392	2.322	0.750	0	53.1	63.8	3.3	1.7	16.8	14.4	0.26
PbO	7.193	0.046	350	59.5	0	0.658	0.808	0.128	23.2	45.5	0	1.5	53.0	0	1.17
〃	7.688	0.063	400	87.3	0.317	3.173	0.881	0.029	71.7	43.7	0.5	0.8	52.9	2.1	1.21
〃	7.193	0.046	450	81.6	0.102	2.574	0.518	0.012	75.5	47.5	1.4	2.1	45.3	3.7	0.95
〃	8.195	0.046	500	86.6	0.488	2.600	0.230	0.112	54.8	75.1	1.5	0.8	17.0	5.6	0.23
MnO	8.765	0.047	300	44.0	0.279	0.135	—	—	5.2	87.2	0	0.7	11.7	0.4	—
〃	8.005	0.105	400	77.3	0.037	0.959	0.270	0.370	23.4	91.4	0.2	0.3	7.3	0.8	—
〃	7.798	0.123	450	96.2	0.565	0.291	0.671	0	11.3	77.4	1.1	0.9	12.1	8.5	—

Table 2. Effect of Concentration of Acetaldehyde in the Aqueous Solution.
(Catalyst 30 cc. ; 30 % Aq. Solution of CH_3CHO 25 cc. ; Rate of Dropping of Aq. Solution of CH_3CHO 10 cc./hr.)

Catalyst	React. Temp. (°C)	Aq. Soln. of CH_3CHO: CH_3CHO (g/10cc.)*	Aq. Soln. of CH_3CHO: CH_3CHO Total (g)	Aq. Soln. of CH_3CHO: CH_3COOH (g)	Conv. Ratio of CH_3CHO (%)	Products: CH_3COOH (g)	Products: CH_3COCH_3 (g)	Products: CH_3COOEt (g)	Products: EtOH (g)	Yield of CH_3COCH_3 (%)	Gas Analysis (%): CO_2	C_nH_{2n}	CO	H_2	CH_4	H_2/CO_2
ZnO	400	7.810[a]	19.525	0.156	90.2	0.020	1.904	0.607	1.854	16.4	28.2	3.1	3.5	58.6	6.6	2.06
〃	〃	7.014[b]	17.535	0.360	90.0	0.041	2.871	0.881	0.814	27.6	29.9	3.4	2.0	60.1	4.6	2.01
〃	〃	6.483[c]	16.208	0.086	80.6	0.024	2.358	0.890	1.995	27.4	27.1	1.9	7.7	55.7	7.5	2.06
Fe_2O_3	400	7.739[a]	19.348	0.310	53.6	0.019	0.641	1.544	1.427	9.4	33.3	10.0	16.3	20.2	20.2	0.61
〃	〃	7.059[b]	17.648	0.173	50.8	0.094	1.055	1.860	1.332	17.9	31.9	0.8	15.5	38.9	12.9	1.22
〃	〃	6.321[c]	15.803	0.123	65.3	0.080	1.341	1.617	2.211	19.6	33.0	1.2	3.3	56.0	6.5	1.70
CaO	400	7.809[a]	19.523	0.194	92.2	0	2.461	0.550	3.973	20.7	2.4	0.4	9.2	70.5	17.5	—
ZnO	450	1.155	2.888	0.026	90.1	0	1.370	0.020	0.077	79.3	39.2	0	1.0	59.8	0	1.53
〃	〃	2.696	6.740	0.089	98.0	0	3.467	0.170	0.792	79.6	31.1	1.1	1.1	62.7	4.0	2.01
〃	〃	3.261	8.040	0.166	92.4	0.022	3.833	0.315	0.665	78.2	32.3	1.2	0.9	63.2	2.4	2.06

* CH_3CHO g/aq. soln. of CH_3CHO 10 cc.
[a] Pure CH_3CHO
[b] Mole ratio of CH_3CHO to H_2O 2 : 1
[c] Mole ratio of CH_3CHO to H_2O 1 : 1

Table 3. Effect of the Rate of Dropping of the Aqueous Solution of Acetaldehyde.
(Catalyst 30 cc. ; Reaction Temperature 450°C ; 30 % Aq. Solution of CH_3CHO 25 cc.)

Catalyst	Aq. Soln. of CH_3CHO: CH_3CHO (g)	Aq. Soln. of CH_3CHO: CH_3COOH (g)	Rate of Dropping (cc/hr)	Conv. Ratio of CH_3CHO (%)	Products: CH_3COOH (g)	Products: CH_3COCH_3 (g)	Products: CH_3COOEt (g)	Products: EtOH (g)	Yield of CH_3COCH_3 (%)	Gas Analysis (%): CO_2	C_nH_{2n}	CO	H_2	CH_4	H_2/CO_2
ZnO	6.780	0.123	5	98.4	0.041	2.279	0.291	0.405	51.8	34.1	0.9	1.5	60.8	2.7	1.78
〃	6.740	0.089	10	98.0	0	3.467	0.170	0.792	79.6	31.1	1.1	1.1	62.7	4.0	2.01
〃	6.443	0.137	20	86.3	0.069	2.426	0.437	0.664	66.2	31.1	1.0	1.0	64.8	2.1	2.08

Fe_2O_3, or CaO, and at 400°C, the effects of some high concentrations of acetaldehyde (pure acetaldyde ; mole ratio of acetaldehyde to water is 2 : 1 or 1 : 1) were investigated.

ZnO : With pure acetaldehyde, the conversion ratio was 90%, while the yield of acetone was only 16%. When the mole ratio of acetaldehyde to water was 2 : 1 or 1 : 1, the yield of acetone was 27%.

Fe_2O_3 : With pure acetaldehyde, the conversion ratio was 53% and the yield of acetone was only 9%. The larger the amount of water in the aqueous solution was, the higher yield of acetone was obtained, and the ratio of H_2 to CO_2 in the formed gas increased from 0.61 to 1.70. As the content of CH_4 and CO was large in every case, it seems that the decomposition of acetaldehyde occurred considerably.

CaO : With pure acetaldehyde, the conversion ratio was 92% and the yield of acetone was 20%. Acetic acid was not found and the yield of ethyl alcohol was 25 % and higher than with other catalysts.

(ii) Effect of low concentration of acetaldehyde. With the catalyst of ZnO, at 450°C, and at the rate of dropping of 10 cc./hr., the effects of some low concentrations of acetaldehyde in the aqueous solution (1 g./10cc., 2.7 g./10cc., 3.2 g./10cc.) were compared. In each low concentration, the conversion ratio was above 90%, the yield of acetone was 78-79% and the ratio of H_2 to CO_2 was about 2. With the concentration lower than 3 g./10 cc., therefore, the effect of concentration of acetaldehyde upon the yield of acetone was hardly found. The above-mentioned results show that the optimum concentration of acetaldehyde is lower than 3 g./10 cc.

3. Effect of the rate of dropping of the aqueous solution of acetaldehyde.

With ZnO, and the concentration of 3 g. CH_3CHO/10 cc.aq.soln. and at 450°C, the effects of some rates of dropping (5 cc./hr., 10 cc./hr., 20 cc./hr.) were compared.

In Table 3 is shown the effect of the rate of dropping.

The conversion ratio was 98%, both at 5 cc./hr. and 10 cc./hr., but at 20 cc./hr., decreased to 86%. The yield of acetone was the maximum of 79% at 10 cc./hr., 66% at 20 cc./hr., and 51% at 5 cc./hr. Therefore, it was found that the optimum rate of dropping is 10 cc./hr.

SUMMARY

In the synthesis of acetone from acetone and water in vapor phase, ZnO or Fe_2O_3 was the best catalyst, followed by CdO or PbO.

The concentration of acetaldehyde lower than 3 g./10 cc., the reaction temperature of 400-450°C, ane the rate of dropping of 10 cc./hr. were found to be in optimum reaction conditions.

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REFERENCES

(1) This investigation was done at Nodzu Laboratory in 1947, and was read before the meeting of the Uuion of Engineering Societies in Kansai (October 10, 1952).

(2) Part 3 : 'On Catalysis' (T.Isoshima, this Bulletin, **32**, 159 (1954)).

(3) Part 2 : 'Quantitative analysis of the mixture of acetic acid, acetaldehyde, acetone, ethyl acetate, and ethyl alcohol' is in press. T. Isoshima, (*J. Chem. Soc. Japan* (Ind. Chem. Section) **57**, 745 (1954)).