

# STUDIES ON THE CATALYTIC FORMATION OF DIOLEFINS FROM MONO-OLEFINS.

## PART II. POISONING AND PROMOTION OF CHROMIUM OXIDE CATALYSTS IN THE DEHYDROGENATION OF MONO-OLEFINS TO DIOLEFINS.

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### ABSTRACT.

The influence of water vapour, sodium vapour, sulphur and phosphorus pentoxide in the catalytic activity of chromium oxide catalysts in the dehydrogenation of butenes to butadienes, has been studied.

According to Beeck (1935) no dehydrogenation of paraffins, olefins and alcohols takes place unless traces of water are present in the vapour concerned. He postulates that this water is necessary to maintain a mono-molecular layer of water on the catalyst surface and this layer is the true seat of dehydrogenation. He had also some experimental evidences showing that water can be substituted by certain other molecules having hydrogen bond with electronegative elements like  $H_2S$ . Another important observation recently made by Taylor and co-workers (1939) relates to the effect of water vapour on the dehydrogenation activity of chromium oxide catalyst which brings about ring closures of paraffins and olefins having six or more carbon atoms in the chain, to aromatic hydrocarbons. Taylor finds that water vapour which is strongly absorbed by chromic oxide is a marked poison to this reaction. For example, the introduction of 3% water with a standard heptane feed of 0.3 c.c./15 g. catalyst decreased the rate of gas evolution to one-fifth of the normal rate. The effect was reversible and on elimination of water vapour from the inlet stream, progressive restoration of the catalyst activity occurred as the water was desorbed from the catalyst.

The present paper describes experiments that were undertaken to study the following factors which considerably influence the activity of chromic oxide catalyst in the dehydrogenation of mono-olefins to diolefins:—

1. Effect of removal of adsorbed water.
2. Effect of addition of sodium vapour and phosphorus pentoxide.
3. Effect of sulphur.
4. Effect of addition of water.
5. Temporary poisoning removable by treatment with hydrogen.

*Effect of removal of adsorbed water:* Experiments were conducted in the apparatus described in Part I (Fig. 1).  $Cr_2O_3-Al_2O_3$  (5%) free from sulphur and other impurities was used. It was prepared by the method described in Part I. For obtaining sulphur free chromium nitrate, pure ammonium dichromate was first converted to chromic acid by treatment with nitric acid. This was then reduced by alcohol to hydroxide (Turkevich, Fahrner and Taylor, 1941), which on treatment with nitric acid gave pure chromium nitrate.

Butene, dried over metallic sodium was dehydrogenated over this catalyst at 500°C. and 15 mm. of Hg. The gaseous reaction products were collected in the liquid air trap for half an hour at intervals of about 7 hours, and before taking each such observation the catalyst was heated for a period of about 6 hours at 600°C. and 0.2–0.5 mm. of Hg to effect a progressive removal of adsorbed water from the catalyst. The results of the experiments are given in Table I.

TABLE I.

Catalyst:  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$  (5%).Conditions: Catalyst volume = 10.5 c.c. Initial period of drying of the catalyst in  $\text{H}_2$  at  $550^\circ\text{C}$ . = 10 hours

No.	Temp. $^\circ\text{C}$ .	Pressure in mm.	Space velocity.	Drying period in hours.	Yield of butadiene.
1	500	15	27.5	7	30.8
2	500	15	29.2	14	28.3
3	500	15	27.0	20.5	24.5
4	500	15	28.3	27.0	20.7
5	500	15	30.5	33.0	14.2
6	500	15	29.1	39.0	11.3

Results shown in Table I, indicate a gradual decrease in the yield of butadiene-1,3 with progressive drying of the catalyst. Thus on drying the catalyst for a period of about 40 hours at  $600^\circ\text{C}$ . and 0.2-0.5 mm. of Hg the yield of butadiene decreased to one-third its original value. It was further observed that in experiments No. 5 and 6, some polymerised products were formed. This shows that the removal of adsorbed water promotes occurrence of secondary reactions leading to the formation of polymerised products.

*Effect of sodium vapour and phosphorus pentoxide:* Metallic sodium and phosphoric acid are powerful polymerising agents, specially for butadiene and butene. The effect of the presence of these in the dehydrogenation of butene over  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$  catalyst has been studied with a view to finding out whether simultaneous dehydrogenation and polymerisation reactions can be effected.

Butene, dried over metallic sodium, was passed over molten sodium, kept as near the reaction tube as possible. The gas carrying only very small amounts of sodium vapour was dehydrogenated at  $500^\circ\text{C}$ . and 15-30 mm. pressure over  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$  catalyst. The results are given in Table II.

TABLE II.

No.	Temp. $^\circ\text{C}$ .	Pressure in mm.	Degree of dissociation of butene.
1	500	15	0.44
2	500	18	0.42
3	500	26	0.36
4	500	36	0.32
5	500	40	0.29

From the results shown in Table II, it will be observed that the introduction of small amounts of sodium vapour with the butene feed did not affect the degree of dissociation. The fact that the degree of dissociation varied almost inversely as the reaction pressure indicates that activity of the catalyst remained steady. It was expected that sodium vapour might initiate polymerisation of butene-butadiene to a certain extent but no such reaction was observed. To the same catalyst,  $\text{P}_2\text{O}_5$  (10% on the weight of the catalyst) was added, and dehydrogenation of butene carried out. Experiments (Table III) showed that the yield of butadiene is markedly affected but no polymers are formed.

TABLE III.

Experiment No.	Temp. $^\circ\text{C}$ .	Pressure in mm.	Yield of butadiene, %.
1	500	17	26.0
2	520	20	25.5
3	540	23	31.6

*Effect of Sulphur:* It has been found that the presence of small amounts of sulphur in  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$  catalyst has promoting effect in its dehydrogenation activity.  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$  catalyst containing as much as 1.0-1.5% sulphur showed quite good activity but the reaction gases contained appreciable amounts of  $\text{H}_2\text{S}$ .

*Effect of addition of water vapour:* The effect of addition of water vapour in various amounts to butene in the process of its dehydrogenation over  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$  (5%)- $\text{V}_2\text{O}_5$  (2.5%)- $\text{Mo}_2\text{O}_3$  (2.5%) catalyst has been investigated in the apparatus described in Fig. 1 (Part I) with the additional equipment shown in Fig. 2. Data for six experiments are given in Table IV.

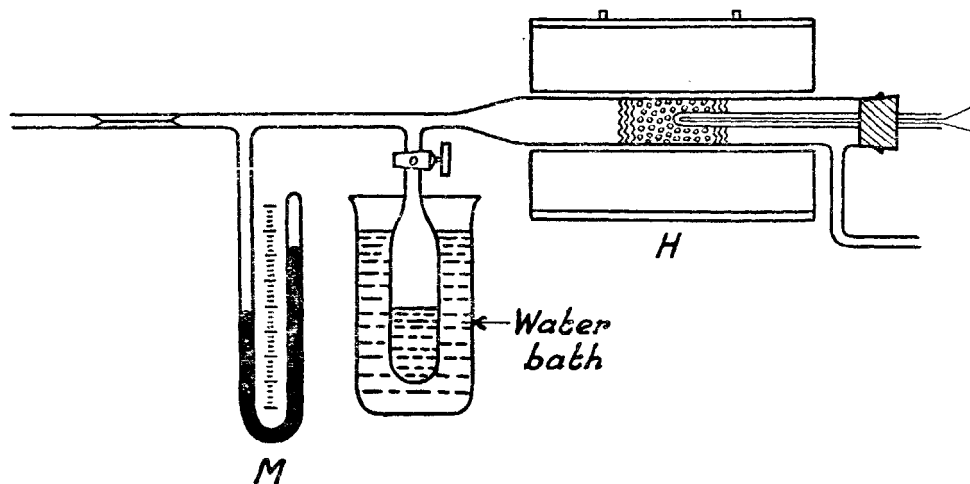


FIG. 2.

From Table IV, it will be seen that use of an equivalent volume of water vapour with butene does not affect the degree of dissociation of butene to butadiene. With larger dilutions the reaction is hindered. This is evidently due to a saturation of the active parts of the catalyst by water vapour. In this set of experiments there was practically no formation of polymerised products. It is thus possible to see that the presence of water vapour in limited amounts may not affect the dehydrogenation activity of chromium oxide catalyst under suitable operating conditions, but may suppress the secondary reactions which lead to the formation of aromatic hydrocarbons from butene.

TABLE IV.

No.	Temp. °C.	Pressure in mm.	Cal. vol. of $\text{H}_2\text{O}$ vapour in c.c. at N.T.P. passed per hour.	Cal. vol. of butene in c.c. at N.T.P. passed per hour.	Space velocity.	Ratio of butene: $\text{H}_2\text{O}$	Degree of dissociation of butene.
1	500	15	nil	287	27.0	nil	0.49
2	500	17	99.3	246	32.6	1 : 0.40	0.48
3	500	19	221	229	42.4	1 : 0.98	0.46
4	500	22	433	203	60.0	1 : 2.10	0.42
5	500	24	517	176	65.3	1 : 2.90	0.30
6	500	26	625	150	73.1	1 : 4.20	0.21

*Temporary poisoning removable by hydrogen:* It has been of much interest to find that when 3-methyl-butene-1 is dehydrogenated over  $\text{Cr}_2\text{O}_3$  gel, particularly at 330-400°C. and 15-30 mm. of Hg. a progressive decrease in the activity of the catalyst occurs with the length of pass. Detailed investigation (to be subsequently described in connection with our studies on the chemical equilibrium in Isoprene formation from 3-methyl-butene-1 at low pressures) revealed

that the deactivation was due to a temporary 'saturation' of the active parts of the catalyst by the unsaturated hydrocarbons and this being reversible, the original activity of the catalyst could be completely restored on treatment with hydrogen at elevated temperatures.

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