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# BENEFICIAL EFFECT OF HYDROGEN CIRCULATION OVER A DEHYDROGENATION CATALYST

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In the direct catalytic conversion of ethanol to ethyl acetate over promoted copper catalysts DOLGOV *et al.*[1] have reported that ester yields are improved by circulating over the catalyst part of the hydrogen formed in the dehydrogenation reaction :

$$\begin{array}{ccccc} 2C_2H_5OH & = & 2CH_3CHO & = & CH_3COOC_2H_5 \\ & & +2H_2 & & +2H_2 \end{array}$$

They have attributed this to the beneficial influence of hydrogen on diffusion coefficients. In gravimetric studies on the catalyst under reaction conditions we have found a different explanation for this.

The experimental set-up was a conventional McBain sorption balance, the lower part of which was provided with an inlet and an outlet. The esterification reaction was carried out over the catalyst taken in the basket of the sorption balance. The weight of the catalyst, undergoing changes under actual reaction conditions, was obtained from the elongation of the quartz spiral as measured by a precision cathetometer (correct to 0.01 mm corresponding to 0.2 mg).

A promoted copper catalyst supported on active carbon, improved by us[2] for the direct esterification of ethanol, was used for the studies. The catalyst was evacuated at 300°C, reduced in a stream of hydrogen for 6 hours and again evacuated to constant weight at that temperature. The temperature was then lowered to 250°C. Dry oxygen-free nitrogen saturated with ethanol (28°C) in a sintered-disc bubbler was passed over the catalyst and the weight of the catalyst was noted as a functtion of time. The exit gas was passed through a trap cooled at −78°C and the condensed products were periodically analysed on a gas chromatograph.

The weight increase of the catalyst cannot be attributed to adsorption of ethanol only, it will be the sum total of all the species existing on the catalyst under reaction conditions. On attaining the steady state the alcohol bubbler was

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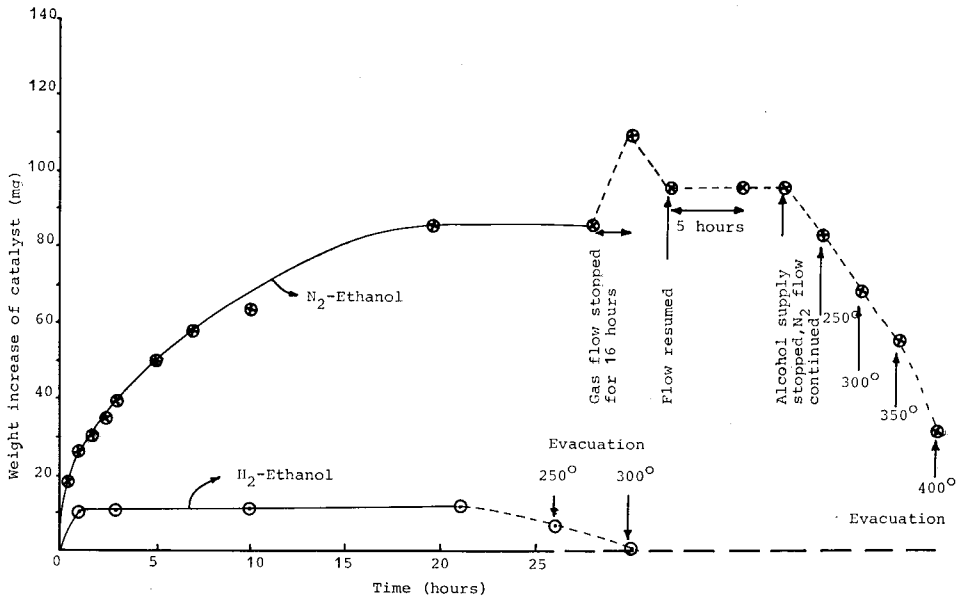


**Fig. 1.** Weight increase of catalyst (initial weight 1.19 g) in $N_2$-ethanol and $H_2$-ethanol streams at 250°C.

removed and the nitrogen flow continued. Later the catalyst was evacuated in stages at 250, 300, 350 and 400°C, noting the steady weight at the end of every step. The experiment was also conducted with hydrogen, instead of nitrogen, as the carrier gas for the alcohol vapour. The results are shown in Fig. 1.

With nitrogen as carrier, the weight of the catalyst goes on increasing and reaches a steady value at 86 mg above the starting weight (1, 19 g after evacuation and reduction). Static adsorption measurements of ethanol over this catalyst at 250°C without any carrier gas indicate that the increase in weight of the catalyst under these conditions should be only 10–20 mg. Obviously, under flow conditions the catalyst has also picked up a lot of the product formed in the reaction. On stopping the flow for overnight, the product left over in the system is also adsorbed (at 250°C) and the catalyst weight increases by another 24 mg from the steady-state value. Part of this (14 mg) can be swept off from the catalyst on resuming the flow and a new steady-state weight is obtained. No decrease in weight takes place on stopping the supply of alcohol vapour and continuing nitrogen flushing. On progressive evacuation at 250, 300, 350 and 400°C, the weight decreases by 13, 14, 14 and 23 mg respectively.

After evacuation at 400°C for 6 hours, the weight of the catalyst is 32 mg above its starting weight. Hence the products formed on the catalyst in a nitrogen-ethanol flow system cannot be removed even under such drastic conditions and

the catalyst undergoes permanet deterioration.

In striking contrast to this is the behaviour of another sample of the same catalyst when subjected to a flow of hydrogen saturated with ethanol. The weight increase of the catalyst is only 10 mg in the first hour, this increases to 12 mg in the next 21 hours. Evacuation at 250°C removes half of this, at 300°C the whole of it is removed and the original weight of the catalyst is restored. Additional experiments have shown that if the catalyst is once subjected to nitrogen-ethanol stream, its weight can be lowered to some extent in a hydrogen-ethanol stream, but it can no longer be restored to the starting value even by subsequent evacuation at 400°C.

Product analysis does not show any significant difference between the experiments with the two carrier gases.

The marked increase in weight of the catalyst in a nitrogen-ethanol flow system cannot be due to traces of oxygen in the nitrogen oxidizing the copper in the catalyst. Such an oxidation can account for a few mg only, but even that is impossible since the hydrogen formed as product in the dehydrogenation should reduce any copper oxide formed. A blank experiment with nitrogen flow over the catalyst has indeed shown that there is no measurable weight increase. Hence the weight increase observed, the difficulty of its removal and the partly irreversible nature of it will have to be attributed to condensation products (of probably acetaldehyde) over the catalyst under reaction conditions. Aldehydes are well known to form resinous condensation products over catalysts. The use of hydrogen instead of nitrogen as the carrier gas apparently suppresses such condensation, perhaps by readily hydrogenating the unsaturates, which can otherwise condense or polymerise because of their reactive double bonds.

The beneficial effect of hydrogen circulation over the catalyst may be partly due to the changes in diffusion coefficients (especially at higher ethanol vapour pressures and on large-scale operation) as suggested by DOLGOV *et al.*, but the major role of it seems to be in scavenging the catalyst surface and cleaning it of all unwanted potentially polymerisable reactive species. The reproducibility of the weight of the catalyst subjected to the hydrogen-ethanol flow suggests that hydrogen in the feed preserves the catalyst surface and can ensure long life for the catalyst. The slight influence of hydrogen on the backward reaction in the alcohol-aldehyde-ester equilibrium may be more than compensated by the greater life given to the catalyst.

## References

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2) P. G. MENON and J. PRASAD, to be published.