

THE FUNCTION OF THE PROMOTERS IN THE CATALYSTS FOR THE FISCHER-TROPSCH SYNTHESIS.

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It is well known that one of the more effective catalysts for the Fischer-Tropsch synthesis contains cobalt, thoria and kieselguhr in the proportions

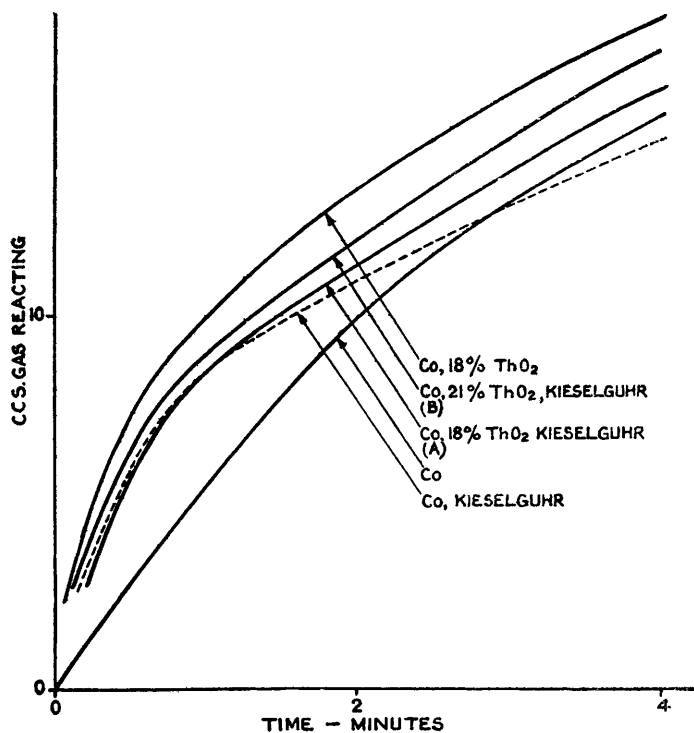


FIG. 1.—The reduction of ethylene at 20° C. by hydrogen per 10 gm. cobalt metal.

100 : 18 : 100, and that this preparation has been discovered by trial and error.¹ Nothing is known about the functions of the thorium and the kieselguhr in this catalyst, and any statements which have appeared on this subject in the literature are no more than speculations. In order to obtain experimental information on this subject the rates of the simple reactions

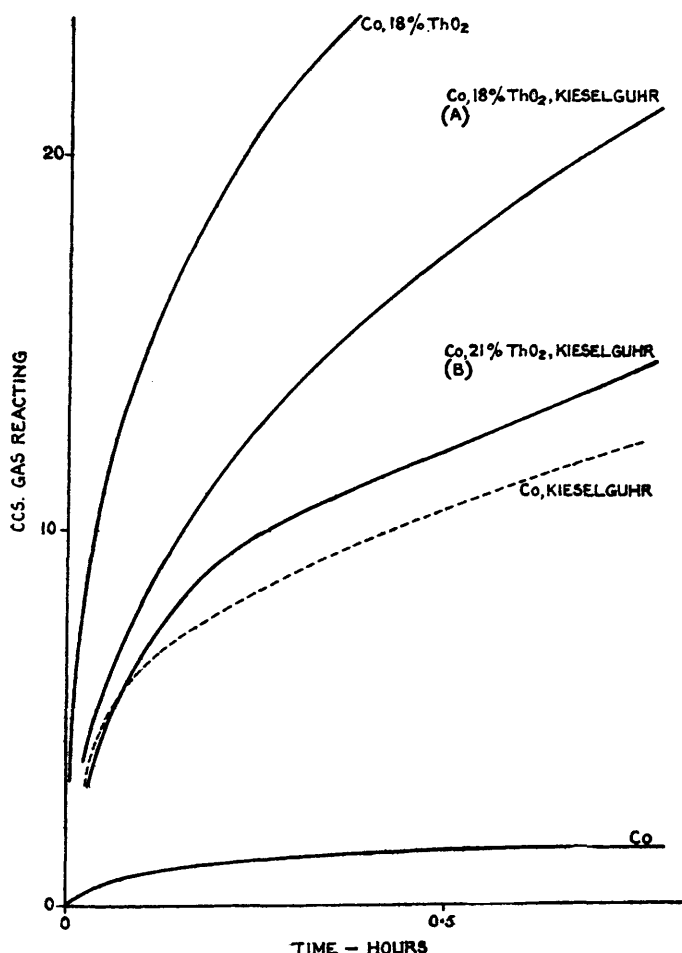


FIG. 2.—The initial fast rate of carbide formation by the reaction
 $2\text{CO} + 2\text{Co} \rightarrow \text{Co}_3\text{C} + \text{CO}_2$ at 200°C .
 and per 10 gm. of cobalt metal.

that form the first stages of the synthesis were determined for the following five catalysts :

- | | |
|-----------------------------------|---|
| (1) Co. | (4) Co-ThO ₂ -Kieselguhr 100 : 18 : 100 (A). |
| (2) Co-ThO ₂ 100 : 18. | (5) Co-ThO ₂ -Kieselguhr 100 : 21 : 100 (B). |
| (3) Co-Kieselguhr 1 : 1. | |

These were all prepared from solutions of the nitrates of cobalt and thorium, to which the kieselguhr had been added, by precipitation with K_2CO_3

¹ Fischer and Koch, *Brennst. Ch.*, 1932, 13, 61.

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solution, heating to boiling, washing and reduction by hydrogen at 375° C. Catalysts (4) and (5), prepared in this way, were provided by the Fuel Research Station, Greenwich, catalyst (4) being an active synthesis catalyst, but catalyst (5) being almost inactive. This difference was not ascribed

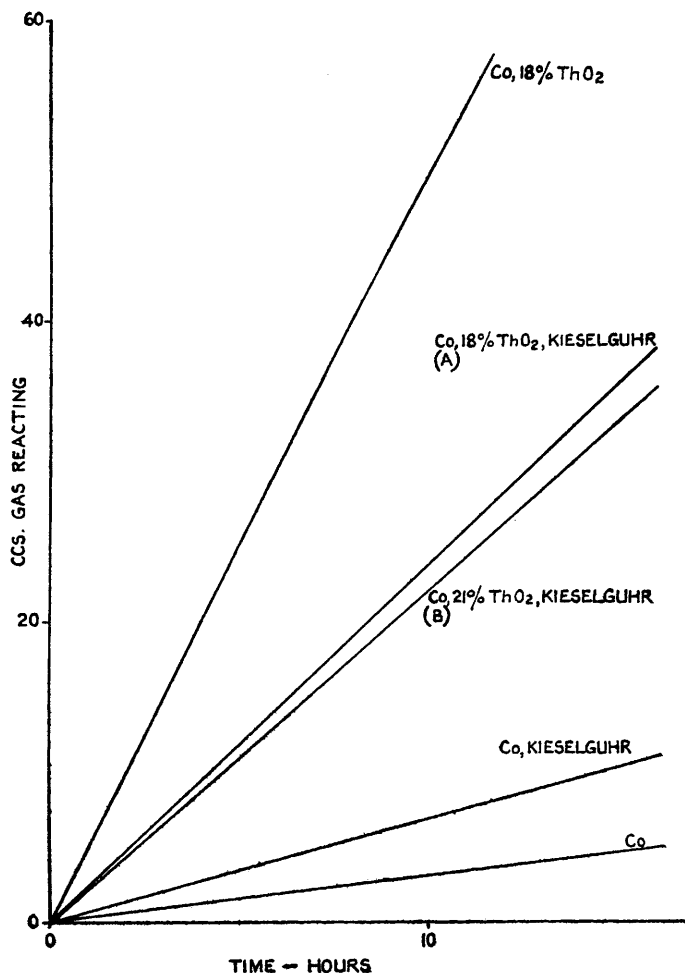
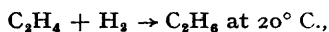


FIG. 3.—The final slow rate of carbide formation by the reaction
 $2\text{CO} + 2\text{Co} \rightarrow \text{Co}_2\text{C} + \text{CO}_2$ at 200° C.
 and per 10 gm. of cobalt metal.

to the slight difference in composition, but to the operation of some uncontrolled factor in the preparation.

All these catalysts were first examined for the reaction



and they gave the surprising result that they were all equally active. This is shown in Fig. 1. The curves for catalysts (2) to (5) are similar and close together, and that for Co alone, although it starts slower, soon reaches the other group of curves. This suggests that the available area of the Co may be the same in all the catalysts, and that neither the thoria

nor the kieselguhr causes an increased dispersion of the cobalt. It also shows that for the reduction of olefines neither thoria nor kieselguhr is a specific promoter. And finally the fact that catalyst (5) is as good a catalyst for the hydrogenation as the others shows that no gross accident can have happened during its preparation, because the usual catalyst poisons stop the hydrogenation of ethylene very easily.

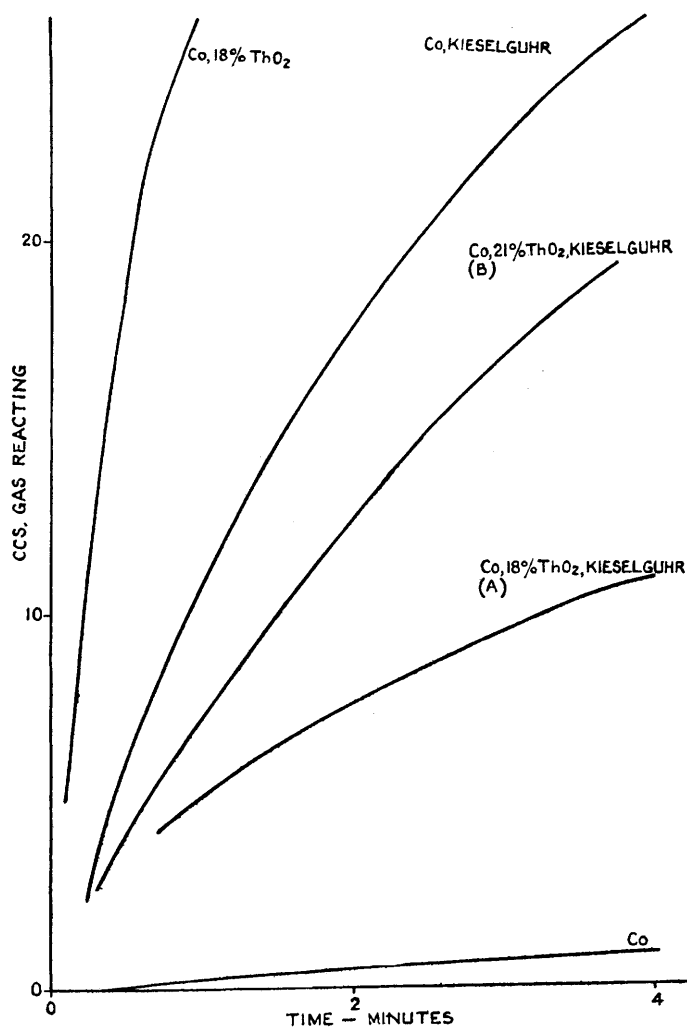


FIG. 4.—The reduction of cobalt carbide by hydrogen per 10 gm. cobalt metal at 180° C.

Figs. 2 and 3 show the effect of the same promoters on the rate of carbide formation by the reaction $2\text{CO} + 2\text{Co} = \text{Co}_2\text{C} + \text{CO}_2$. The curves indicate that both kieselguhr and thoria are powerful specific promoters for this reaction, that the most effective catalyst is that containing 18 % ThO₂ and no kieselguhr, and that catalyst (5) with 21 % ThO₂ reacts very much more slowly than the active Fischer catalyst with 18 % ThO₂, both containing kieselguhr. The final slow rates of formation of carbide

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by the same reaction show the same differences, although here the activity of catalyst (5) is not a great deal below that of catalyst (4).

The rate of reaction of hydrogen with cobalt carbide to give methane, presumably by way of $-\text{CH}_3$ groups, is shown by the curves of Fig. 4. These show that again both thoria and kieselguhr are powerful promoters for the reduction. They also give the striking result that of all the catalysts used, with the exception of pure cobalt, the active Fischer catalyst with 18 % ThO_2 and 100 % kieselguhr, gives by far the slowest rate of reduction of the carbide. This confirms the previously expressed

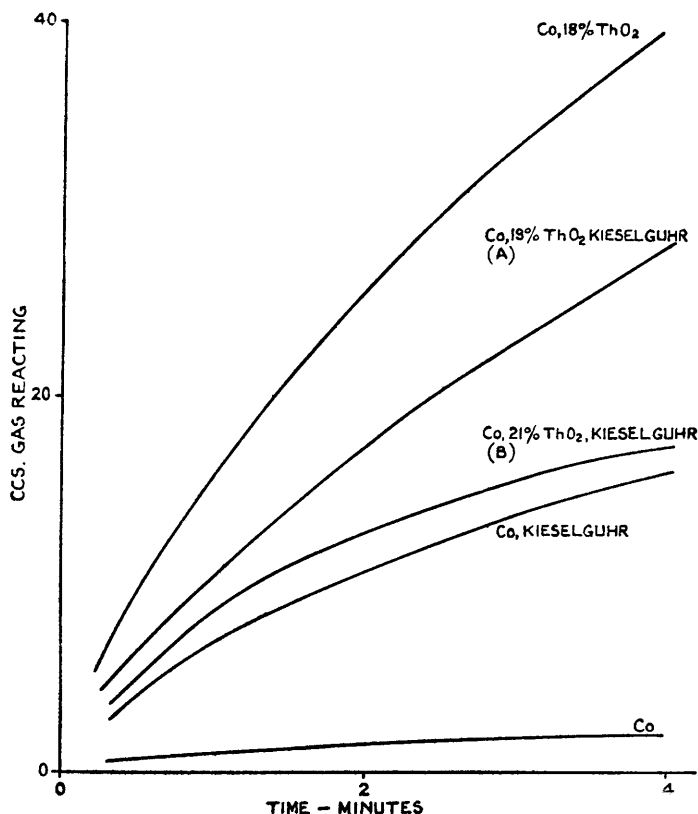


FIG. 5.—The reaction $\text{CO} + 2\text{H}_2$ at 180°C . per 10 gm. cobalt metal.

view² about the mechanism of the Fischer reaction, according to which the rate of formation of carbide by the reaction



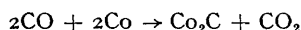
must be faster than the reduction of the carbide, to allow for the accumulation of surface carbide during the reaction, and the consequent exclusion of chemisorbed hydrogen from the surface, if oils are to be formed. Otherwise methane would be the main reaction product. In accordance with this view the present curves show that the only one of the catalysts used which gives good yields of oil in the Fischer synthesis, has a relatively slow rate of carbide reduction and a relatively fast rate of carbide formation. The preparation with Co-ThO_2 100:18 has a very high rate of carbide formation, but is not a good Fischer catalyst because it shows too high a rate of reduction of carbide. It should form a much better Fischer

catalyst than the usual ones if some means were discovered for decreasing the rate of reduction of its carbide by the desired amount. The preparation with Co-ThO₂-Kieselguhr 100 : 21 : 100 is poor in two respects, firstly that its rate of carbide formation is slow compared with the normal active Fischer catalyst, and its rate of carbide reduction is high.

Finally, Fig. 5 shows the corresponding rates of the reaction of CO + 2H₂ on the series of catalysts, and as they may be considered as giving the rate of the reaction



it is satisfactory to find that they lie in the same relative positions as the corresponding curves for the direct formation of carbide by the reaction



given in Fig. 2.

Summary.

(1) In the Fischer catalyst the substances thoria and kieselguhr do not act primarily by increasing the available area of the Co, but as specific promoters for the formation and reduction of cobalt carbide.

(2) The curves obtained show that although the primary consideration for an active Fischer catalyst is a high rate of carbide formation, this must be coupled with a relatively slow rate of reduction of carbide if oils are to be formed.

(3) The results support the theory of the Fischer reaction previously advanced.²

This work, which formed part of the programme of the Fuel Research Board of the Department of Scientific and Industrial Research, was carried out during 1939 in the Department of Colloid Science, Cambridge, under the supervision of Professor Rideal, to whom the writer is indebted for constant advice during its progress. This account is published by permission of the Director of Fuel Research.

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*The Fuel Research Station,
Greenwich.*

² Craxford, *Trans. Faraday Soc.*, 1939, **35**, 946. Craxford and Rideal, *J.C.S.*, 1939, 1604.