

ENCLOSURE (B)19

## PART II

## STUDIES ON IRON CATALYST

by

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SUMMARY

Experiments were made to investigate the effectiveness of iron catalysts for synthesis of oil from water gas at normal pressure. Detailed data on these experiments are not now available, but the significant results were as follows:

1. The catalyst Fe-Cu-ThO<sub>2</sub>-MgO-Kieselguhr-K<sub>2</sub>CO<sub>3</sub> (100:20:4:20:175-200:4), prepared by precipitation, was satisfactory at lower reaction temperatures, i.e., 235-240°C.
2. Thorium and magnesium were very effective promoters and served to lower the required reaction temperature.
3. For the purpose of activating the catalyst, it was better to circulate water gas rapidly at the reaction temperature.
4. The yield of synthetic oil with this iron catalyst was 61.6 gm/m<sup>3</sup> of water gas (H<sub>2</sub>:CO=6:4 by volume) at 235°C.

I. INTRODUCTION

Many reports have been made concerning the use of iron catalysts for synthesis of oil from water gas. TSUNODA, MURATA and MAKINO<sup>\*</sup> succeeded in obtaining 83cc of synthetic oil per cubic meter of water gas (H<sub>2</sub>:CO 1:1) at 257°C using the catalyst Fe-Cu-Kieselguhr-K<sub>2</sub>CO<sub>3</sub> (100:25:125:2, by weight). Later they<sup>\*\*</sup> obtained a yield of 88cc of oil using the catalyst Fe-Cu-Mn-Kieselguhr-K<sub>2</sub>CO<sub>3</sub> (100:25:2:125:2), and concluded that manganese was effective as a promoter. They confirmed, too, that magnesia was useful as a promoter, but oxides of uranium and thorium, and especially chromium and aluminium, were poisonous.

Generally, it was believed that for iron-catalyst,<sup>\*</sup> addition of copper was absolutely necessary,<sup>\*\*</sup> and that alkalis were very effective as promoters.

TSUNOKA and his co-workers<sup>†</sup> found a new catalyst, consisting of the above-mentioned catalyst plus boric acid (corresponding to 20% iron content) which gave a yield of 95cc of liquid products per cubic meter water gas (H<sub>2</sub>:CO=2:1) at 240°C.

<sup>\*</sup>J. of Tech. Chem. Japan, 42 (1939) 202

<sup>\*\*</sup>Ibid. 209

<sup>†</sup>Rept. of Kyoto Chem. Research Inst. 10 (1939) 2.

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However, the required reaction temperature was high for commercial usage, and moreover, boric acid is not manufactured on a large scale in Japan. The following experiments were made primarily to find a catalyst without such weak points as these.

## II. DESCRIPTION

The test apparatus was the same as described in Part I of "Studies on Fischer-Tropsch Synthesis". Catalysts were prepared by precipitation from nitrate mixtures and sodium carbonate solutions similar to the procedure for cobalt catalyst as described in Part I, except that the sodium or potassium carbonate was added after washing of the precipitates and before drying.

The following series of experiments were made:

1. The influence of metals or metallic oxides on the catalytic activity of the catalyst Fe-Cu-Kieselguhr- $\text{Na}_2\text{CO}_3$  (100:20:200:4) was investigated.

Mn, Cr, Zn,  $\text{ThO}_2$ ,  $\text{U}_3\text{O}_8$ ,  $\text{Al}_2\text{O}_3$  and MgO were tested as promoters, and it was observed that  $\text{ThO}_2$ , MgO and  $\text{Al}_2\text{O}_3$  were effective in lowering reaction temperature, but Mn and Cr were poisonous.

2. The influence of metals or metallic oxides on the catalytic effect of the catalyst Fe-Cu- $\text{ThO}_2$ -Kieselguhr- $\text{Na}_2\text{CO}_3$  (100:20:4:200:4) was investigated.

Mn, Cr, Zn,  $\text{Al}_2\text{O}_3$  and MgO were tested as promoters, and it was observed that MgO or  $\text{Al}_2\text{O}_3$  was effective, especially the former.

3. Studies were made to determine the effect of varying thorium and magnesia contents on Fe-Cu- $\text{ThO}_2$ -MgO-Kieselguhr- $\text{Na}_2\text{CO}_3$  catalyst.

$\text{ThO}_2$  and MgO were varied over the range of 4 to 30 wt. % (of iron) and a catalyst of the composition 100:20:4:20:200:4 gave the best results.

4. A study was made of the effect of the types of alkalies used, and it was concluded that, sodium carbonate was the best to use in the precipitation step, but 4 % of potassium carbonate was the best alkali promoter for the above-mentioned iron catalyst.

5. The amount of Kieselguhr in standard iron catalyst Fe-Cu- $\text{ThO}_2$ -MgO-Kieselguhr- $\text{K}_2\text{CO}_3$  was varied from 125 to 300 % of iron by weight, and it was found that the best content was 175-200 %.

6. The primary activation of the iron catalyst is accomplished by reduction with water gas. Experiments were made to investigate the effect of the rate of circulation (increased gas velocity) on rate of activation. The advantage of rapid circulation in decreasing reduction time is shown by Table V(B)19.

7. After the activation, as described in the preceding paragraph, a single-stage conversion test was made using water gas ( $\text{H}_2$  100-61%) at 235°C, atmospheric pressure, and gas velocity of 41/hr. 40cc of the catalyst, Fe-Cu- $\text{ThO}_2$ -MgO-Kieselguhr- $\text{K}_2\text{CO}_3$  (100:20:4:20:200:4) were used. The average yield of liquid hydrocarbons was 61.6 gm/m<sup>3</sup> feed gas over a 50 hour reaction period.

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Table V(B)19  
EFFECT OF CIRCULATION ON VOLUME % DECREASE OF  
WATER GAS USED IN ACTIVATION OF STANDARD IRON CATALYST

Reduction Time (hr)	6	8	12	16	18	22	24	26	Remarks
No. Circulation			18.6	21.7	26.5	30.1	32.5	32.5	gas vel., 41/hr.
Circulation	24.7	31.3	37.4	41.0	42.2	45.2	45.2	45.2	circulated gas vel. 201/hr.