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STUDIES ON THE
FISCHER-TROPSCH SYNTHESIS
(In Three Parts)

by

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Research Period: 1940-1941

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PART I

ACTIVATION OF COBALT
CATALYST BY HYDROGENATION

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SUMMARY

Experiments were made to determine the best conditions for activation of the Standard Fischer-Tropsch cobalt catalyst employed for synthesis of oil from water gas.

The results disclosed that activation by hydrogen gas was excellent for Co-MgO-ThO$_2$-Kieselguhr catalyst (100:8:3:200 by weight), under conditions of 375-380°C, over 2500 gas space velocity and 1 1/2-2 hours reaction time. It was shown, for this case that about 50% of the cobalt in the reduced catalyst was in metallic state, and the catalytic activity was also strongest in this instance.

It was also found that when the above catalyst was used for the synthesis of oil at normal pressure and 175-390°C, a gas contraction of 85% and a yield of over 160cc of oil (sp. gr. about 0.75) for each cubic meter of pure water gas (H$_2$:CO = 2:1 in volume ratio), were obtained.

I.   INTRODUCTION

F. Fischer & H. Koch[*] reported that in the case of a Co-ThO$_2$-Kieselguhr (100: 18:150) catalyst, reduction with hydrogen gas occurs only slightly at 300°C, and the most suitable temperature is 350°C with a reaction time of 4-5 hours. No research data had been reported on the activation of the Co-MgO-ThO$_2$-Kieselguhr catalyst in which magnesia replaced part of the rare thoria. In these experiments the effects of the reduction period and hydrogen gas velocity, in, the temperature range of 375-380°C, on activation of the latter catalyst were studied.

II.   DETAILED DESCRIPTION

A.   Test Apparatus and Procedure

Figure 1(B)19 shows the test apparatus used. The contact oven, which was the chief part of this apparatus consisted of an aluminium block (90mm in diameter and 500mm in length) electrically heated, and through it, 4 reaction tubes were placed in parallel.

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* Brennstoff-Chemie 13, 67 (1932).

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Pure water gas, free from sulphur compounds, was made by blending electro-
lytic hydrogen with carbon monixide produced from formic acid and concen-
trated sulphuric acid.

To make the cobalt catalyst, 61.7 gm of $Co(NO_3)_2 \cdot 6H_2O$, 12.7 gm of $Mg(NO_3)_2 \cdot$
$6H_2O$ and 0.78 gm of $Th(NO_3)_4 \cdot 4H_2O$ were dissolved in 250cc of distilled
water, and mixed by stirring with 350cc of a solution containing 33.6 gm
of Na_2CO_3.25 gm of Kieselguhr were next added, and the solution was fil-
tered. The precipitate was washed with 1500cc of distilled water, dried
and made into tablets 1-3mm in diameter. This catalyst had the approxi-
mate composition of Co-MgO-ThO2-Kieselguhr 100:8:3:200 (by weight); the
metals being mainly carbonates.

About 40cc of catalyst (corresponding to 4 gm of cobalt as metal) were
introduced into the glass tube. After reduction with hydrogen, water gas
was passed through at a velocity of 4 lit/hr (corresponding to a gas space
velocity of 100) and a temperature of 375-380°C.

B.   Experimental Results

1.   The influence of reduction conditions, (varying hydrogen gas
velocity and reduction time, but using a constant total volume of
hydrogen) on catalytic activity is shown in Table I(B)19.

From the data it is noted that the catalyst which was reduced in
the shortest time, showed the strongest activity.

2.   The influence of reduction time on the catalytic activity,
when the space velocity was held constant at 3750, is shown in
Table II(B)19.

From these data it is noted that the optimum reduction period for
3750 SV is 1 1/2-2 hours.

3.   The influence of hydrogen gas velocity on the catalytic ac-
tivity is shown in Table III(B)19. In this experiment, the reduc-
tion time was held constant at 1 1/2 hours.

From these data, it is indicated that the optimum hydrogen gas space
velocity was 3750-2500 for a reduction period of 1 1/2 hours.

4.   It was clear that the catalyst prepared by precipitation
achieved its activity for oil synthesis only after suitable treatment
with hydrogen. To determine the optimum degree of reduction the
following apparatus was devised. (See Figure 2(B)19).

Bottle "B" and the glass tube to 3-way cock "d" were filled with
water from "F". "A" was an Erlenmeyer flask (about 100cc), in which
about 2 grams of reduced catalyst had been placed, avoiding exposure
to air.

Nitrogen gas was introduced at cock "b" and air displaced from flask
"A". The nitrogen gas pressure in the apparatus was brought to at-
mospheric pressure.

Dilute sulphuric acid (1:1) was dripped into "A" from the burette
"D". Hydrogen gas was evolved from the metallic cobalt and carbon
dioxide gas from the carbonate mixtures. Both gases flowed to "B"
through "c" and the water in "B" was drawn off to "C" through cock
"e". To complete the reactions, the flask was heated gently, and

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then cooled to room temperature. The pressure in the apparatus was brought to atmospheric and the volume of water which flowed into "C" was measured.

Next, gases in "A" were displaced into "B" by adding water from "D", the gases in "B" were analyzed, and the amounts of CO_2 and H_2 generated from 1 gram of reduced catalyst were calculated. Experimental results for the catalysts described in Table II(B)19 are given in Table IV(B)19.

In the case of the most effective catalyst, 1.1/2 hours reduction time, 1 gram contained 0.3234 grams of cobalt by actual analysis. Therefore, the maximum hydrogen evolution from 1 gram of catalyst was,

$$22,400 \times \frac{0.3234}{58.94} \doteq 123 \ (cc)$$

But the actual hydrogen gas evolution was only 58.7 cc. Therefore, the reduction degree was,

$$\frac{58.7}{123} \times 100 = 48.0 \ (\%)$$

It is apparent that the effective state of the cobalt catalyst did not contain only highly reduced cobalt metal, but lower oxides of cobalt were also present.

Table I(B)19
INFLUENCE OF REDUCTION CONDITION ON CATALYTIC ACTIVITY

	Temp. of Synthesis ($^{\circ}$C)					Reduction Conditions*	
Temp. of Synthesis($^{\circ}$C)	176	185	190	195	200		
Time of Synthesis(hr)	$8\frac{1}{2}$	$6\frac{1}{2}$	$6\frac{1}{2}$	$8\frac{1}{2}$	9		
Gas Purity (%)	98.4	96.0	98.4	97.8	98.2		
Gas Composition(H_2:CO)	2.03	2.09	2.02	1.97	1.97		
Average Yield (1)	114.9	164.5	149.3	118.6	83.0	SV R.T.	1500, 1 hr
of Synthesis Oil (2)	103.5	160.2	155.6	124.8	91.5	SV R.T.	3750, 2 hr
cc/m^3 (3)	127.0	135.0	121.1	106.5	77.4	SV R.T.	2500, 3 hr

*SV   Space Vol.
 R.T.   Reduct Time

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Table II(B)19
INFLUENCE OF REDUCTION TIME ON CATALYTIC ACTIVITY

		Temp. of Synthesis (°C)				Reduction Conditions*
		175	180	185	190	195	
Time of Synthesis(hr)		7	9	6	7½	8	
Gas Purity(%)		95.4	97.2	95.4	97.8	97.5	
Gas Composition(H$_2$:CO)		2.13	1.06	2.09	1.98	2.02	
Average	(1)	102.0 (86.2)	124.2 (87.0)	149.7 (86.2)	151.7 (83.7)	136.0 (83.3)	R.T. = 1 hr
Yield of Synthesis Oil	(2)	102.0 (86.5)	130.5 (88.5)	165.5 (87.0)	160.3 (87.0)	125.0 (84.0)	R.T. = 1½ hr
cc/m^3	(3)	105.9 (87.4)	135.9 (87.4)	162.9 (86.8)	158.5 (86.8)	124.7 (82.6)	R.T. = 2 hr
(Gas contraction, vol %)	(4)	91.4 (75.4)	118.4 (81.4)	127.7 (74.2)	121.4 (75.2)	116.2 (75.6)	R.T. = 3hr

*SV = 3750

Table III(B)19
INFLUENCE OF HYDROGEN GAS VELOCITY ON CATALYTIC ACTIVITY

		Temp. of Synthesis (°C)					Reduction Conditions*
		175	180	185	190	195	
Time of Synthesis(hr)		8	6½	6½	6	7	
Gas Purity(%)		93.9	96.6	97.5	96.9	98.4	
Gas Composition(H$_2$:CO)		2.15	1.88	2.05	2.07	2.01	
	(1)	113.8 (86.7)	121.7 (87.9)	151.8 (87.9)	148.5 (86.7)		SV = 3750
	(2)	107.0 (86.2)	116.8 (86.9)	149.7 (87.3)	148.5 (86.1)	138.0 (85.3)	SV = 2500
	(3)	100.4 (88.0)	102.8 (82.1)	107.7 (85.1)	120.5 (85.2)	115.9 (85.2)	SV = 1250
	(4)	87.2 (70.3)	100.7 (75.3)		101.3 (82.1)	115.9 (85.2)	SV = 250

*R.T. = 1.5 hr

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Table IV(B)
GASES EVOLVED FROM REDUCED CATALYST

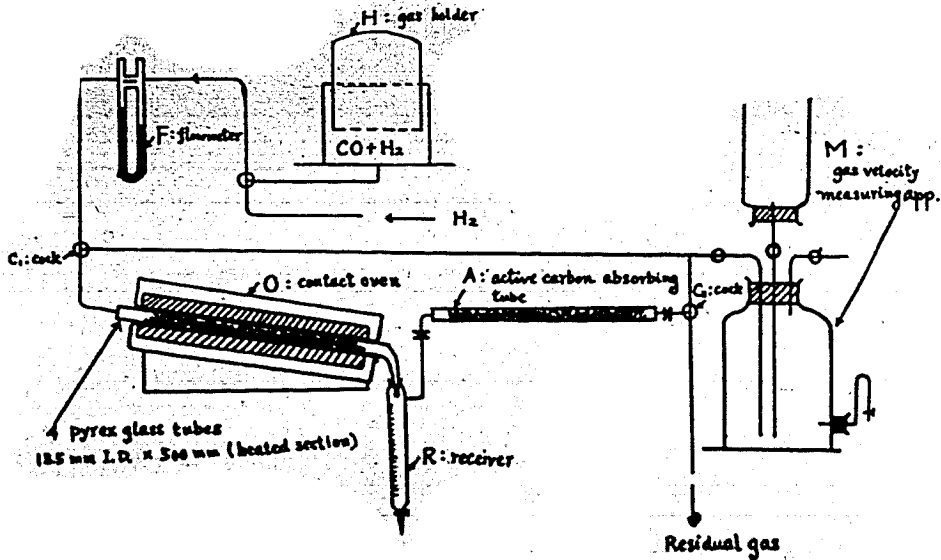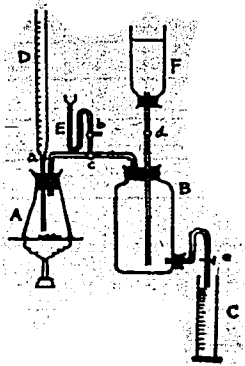| Reduction Time (hr)	Wt. of Cobalt in 1 gram Reduced Cat.	cc of Gas Evolved From 1 gm Red. Cat.		Reduction of Cobalt (%)
		CO_2	H_2	
1.5	0.3234	1.0	58.7	48
2	0.3196	1.0	74.7	62
3	0.8108	0.8	82.3	70

Figure 1(B)19
CATALYST TESTING APPARATUS

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Figure 2(B)19
APPARATUS FOR DETERMINING
DEGREE OF CATALYST REDUCTION