

A COMPARATIVE STUDY OF OIL-SLURRY PROCESS TO FIXED-BED PROCESS
IN THE FISCHER-TROPSCH SYNTHESIS

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§ INTRODUCTION A variety of products are formed in the Fischer-Tropsch (F-T) synthesis, in which the most important nature related to the product selectivity will be the C-number distribution. The C-number distribution of products is intrinsically regulated by the two competing surface reactions. One is the hydrogenative desorption of surface intermediates and the other is the C-C chain growth probably through the CO insertions to the intermediates (1). The former reaction whose activation energy is expected to be higher than the latter will be considerably accelerated when any super-heated spot is created on the catalyst surface.

The oil-slurry process which was originated by H. Köbel (2) is known to have several distinguishing process features; e.g., the process can be operated with the synthesis gas of high CO/H₂ ratios, the catalyst shows high activity based on the unit weight, products are rich in 1-olefins and their C-number distribution can be controlled flexibly, etc.

Differences between the oil-slurry process and the fixed-bed process on catalyst activity and C₁-C₄ product selectivity are described in this paper, by use of the same precipitated iron catalyst and at 200-250°C. The other operating conditions were not standardized between the two processes. Characteristic operating conditions for the oil-slurry process, e.g., milling of the catalyst in oil, the method of catalyst reduction, CO/H₂ ratio of the inlet gas, etc., were kept as recommended by the process founder. Unique pretreatment procedures were adopted for the reduction of catalyst in the fixed-bed process as described in the following section. This method enabled us to prepare catalysts possessing the designated iron carbide contents in the fixed-bed process. A high catalyst activity and a depressed CH₄ formation obtained in the oil-slurry process were in line with those attained in the fixed-bed process when it was operated with the catalyst having low iron carbide contents. Thus, it has become clear that the characteristic features of oil-slurry process arise from the depressed iron carbide formation during the synthesis probably due to the low fugacity of CO on the catalyst surface.

§ EXPERIMENTAL A precipitated iron catalyst, the composition of which was 100Fe : 0.3Cu : 0.6K₂CO₃ by weight, was employed for all experiments. In the fixed-bed process, 10 g of the dried, unreduced catalyst grain of 2-3 mm diameters was packed at the center of a stainless steel block reactor of 10 mm I.D. and 300 mm height. The dried, unreduced catalyst was pretreated successively under atmospheric pressure with 1) air at 320°C for 6 hours, 2) CO at 270°C for 24 hours, and 3) H₂ at 270°C for 24 hours or longer. After these pretreatments, the catalyst was subjected to the F-T synthesis at 200-250°C, under atmospheric pressure, by use of the synthesis gas of CO/H₂ molar ratio of 1.0. The catalyst activity was defined as below;

$$k = -(SV) \ln(1-x) \quad 1)$$

k : catalyst activity / dm³ gFe⁻¹ h⁻¹

(SV) : space velocity of synthesis gas / dm³ gFe⁻¹ h⁻¹

x : conversion of CO.

In the oil-slurry process, the dried, unreduced catalyst was mixed with the

Gatsch fraction of the F-T oil and milled until the particle size of catalyst was as small as 1μ . A Fe-content of the oil-slurry was adjusted to about 10% by weight. Dimensions of the reactor were 37 mm I.D. and 1,000 mm height. Suspended catalyst was reduced at 290°C , under 2-10 bar, by introducing the synthesis gas as bubbles at the bottom of the reactor. CO/H_2 molar ratio of the synthesis gas was 1.3-1.6. Completions of the reduction could be noticed by the decrease in CO_2 and the simultaneous increase in CH_4 in the outlet gas. The F-T synthesis takes place in succession by merely lowering the temperature to the designated levels of $200-250^{\circ}\text{C}$. Catalyst activity was defined in the same manner as that of the fixed-bed experiment.

§ RESULTS AND DISCUSSION In the fixed-bed process, a dried, unreduced catalyst, the rough composition of which is $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ neglecting small amounts of Cu and K_2CO_3 , was converted to Fe_2O_3 in the pretreatment 1). In the pretreatment 2), the rate of CO_2 formation was measured against stream hours of CO as shown in Fig. 1. The amount of CO_2 formed in the first sharp peak of Fig. 1 corresponded to the rapid reduction of Fe_2O_3 to Fe_3O_4 , and the second large peak corresponded to the slow reduction of Fe_3O_4 to Fe_2C and the simultaneous formation of a small amount of free carbon. In the successive pretreatment 3) with H_2 , CH_4 was formed as shown in Fig. 2. The formation of CH_4 subsided after 40 hours of H_2 stream. The amount of CH_4 formed within 40 hours corresponded virtually to the amount of Fe_2C formed in the CO pretreatment, thus converting iron carbide to the metallic iron. Accordingly, it would be possible to prepare the catalyst with different iron carbide contents by varying the hours of H_2 pretreatment as indicated in Fig. 2.

In succession to these pretreatments, the catalysts were subjected to the F-T synthesis at 230°C , by streaming atmospheric $\text{CO} + \text{H}_2$ at the constant flow rate of $0.67 / \text{dm}^3\text{gFe} \cdot \text{lh}^{-1}$. As the first-order kinetics was confirmed to be valid for the overall reaction of the synthesis upto 80% conversion of CO, the catalyst activity, k , was defined as it appeared in Equation 1. In Fig. 3, activities of the catalyst with varied iron carbide contents are plotted against stream hours of the F-T synthesis. Catalyst activities decrease rapidly at the initial stage of the synthesis. Clearly, the catalyst with lesser iron carbide contents exhibits higher activity. The fact indicates that the catalyst activity is caused by the existence of the metallic iron, while the carbide carbon plays a role of the poison for the catalyst. This idea coincides with the reported results (3) on the change of catalyst composition during the F-T synthesis. The report denotes that the initial rapid decrease in catalyst activity accompanies the rapid conversion of $\alpha\text{-Fe}$ to Fe_2C .

The $\text{C}_1 - \text{C}_4$ product selectivities obtained in the above experiments are summarized in the bottom three lines of Table I, in terms of formation ratios of C_1 , C_3 , and C_4 hydrocarbons to C_2 hydrocarbons. An iron catalyst in the metallic state suppresses the formation of CH_4 and favors those of C_3 and C_4 hydrocarbons. The activation energy for the synthesis was obtained as 79.1 kJ mol^{-1} within $230 - 242^{\circ}\text{C}$.

Table I $\text{C}_1 - \text{C}_4$ Product Distributions in Fixed-Bed and Oil-Slurry Processes at 230°C

	CH_4	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$	C_3H_8	C_3H_6	$n\text{-C}_4\text{H}_{10}$	$1\text{-C}_4\text{H}_8$
Oil-slurry	142	100	14.2	91.0	9.3	67.9
Fixed-bed						
$\text{Fe}_1\text{C}_0.0$	320	100	11.1	83.1	5.6	40.0
$\text{Fe}_1\text{C}_0.2$	325	100	8.9	77.0	4.7	34.0
$\text{Fe}_1\text{C}_0.5$	395	100	5.9	67.0	-	27.5

In the oil-slurry process, the catalyst activity did not decrease with stream hours. The value of k in $\text{dm}^3\text{gFe}^{-1}\text{h}^{-1}$ was held at the initial high value, as high as the initial k value observed in the fixed-bed process, throughout the whole reaction course of 50 hours. In Fig. 4 are illustrated results of the activity fouling tests in the oil-slurry process, which was conducted by a step-wise temperature shifting method as well as by an insertion of H_2 treatment in the course of the synthesis. Catalyst poisoning by iron carbide formation might not be taking place in the oil-slurry process. The activation energy for the synthesis was as low as 23.4 - 30.6 kJ mol^{-1} , in the oil-slurry process within 200 - 250°C.

The C₁ - C₄ product selectivities obtained in the oil-slurry process are listed in Table I, to be compared with those obtained in the fixed-bed process. The formation of CH_4 was considerably lesser, and C₃ and C₄ formations were dominant. The results again preclude the formation of iron carbide for the catalyst of the oil-slurry process.

As a conclusion of the present study, several characteristic features of the oil-slurry process in the F-T synthesis are summarized in Table II, in comparison with those of the fixed-bed process.

Table II Different Features of Fixed-bed Process to Oil-slurry Process

	Fixed-bed	Oil-slurry
<u>Reaction condition</u>		
Particle size of catalyst	2 - 3 mm	1 μ
Reaction phase	Gas - solid	Gas - liquid - solid
Flow pattern	Plug flow of gas	Complete mixing of oil-slurry
Heat transport	Gas film controlling	Liquid film controlling
CO/H ₂ molar ratio	1.0	1.3 - 1.5
Operating pressure / bar	1.0	2.0 - 10.0
Fugacity of CO on surface	High	Low
<u>Kinetic feature</u>		
Catalyst activity at 230°C / $\text{dm}^3\text{gFe}^{-1}\text{h}^{-1}$	Rapidly decrease from 3.0 - 10.0 to 0.1	Steady around 2.5 - 8.2
Overall activation energy	79.1 kJ mol^{-1}	23.4 - 30.6 kJ mol^{-1}
Reactivation of catalyst with H_2	Reactivated	Independent
Catalyst composition	Iron carbide	Metallic iron
<u>Product selectivity</u>		
CH_4 formation	Rich	Lean
C-number distribution	Wide and fixed	Flexible
Olefinic or paraffinic	Paraffin rich	Olefin rich

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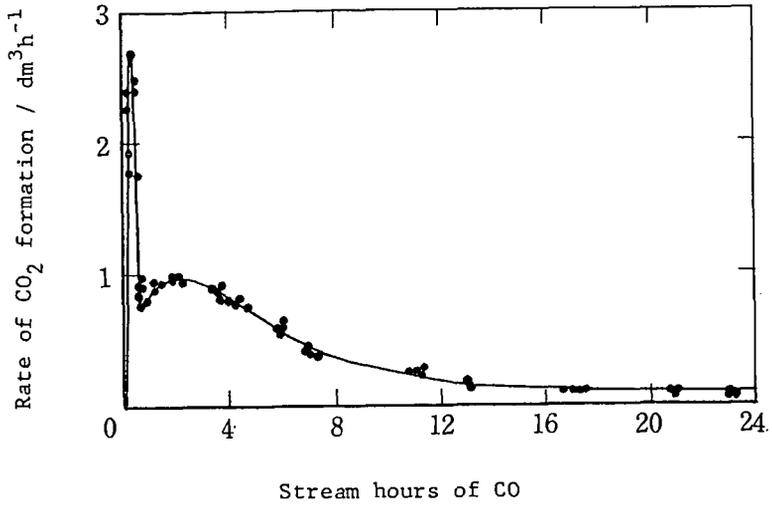


Figure 1 Catalyst Pretreatment 2) in the Fixed-bed Process

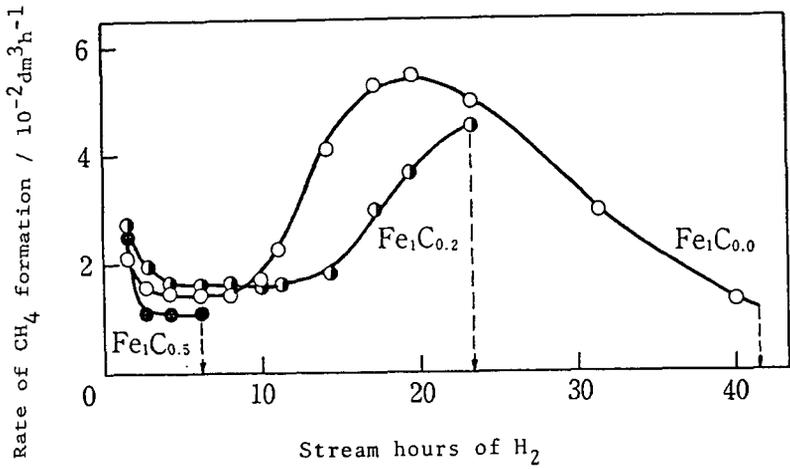


Figure 2 Catalyst Pretreatment 3) in the Fixed-bed Process

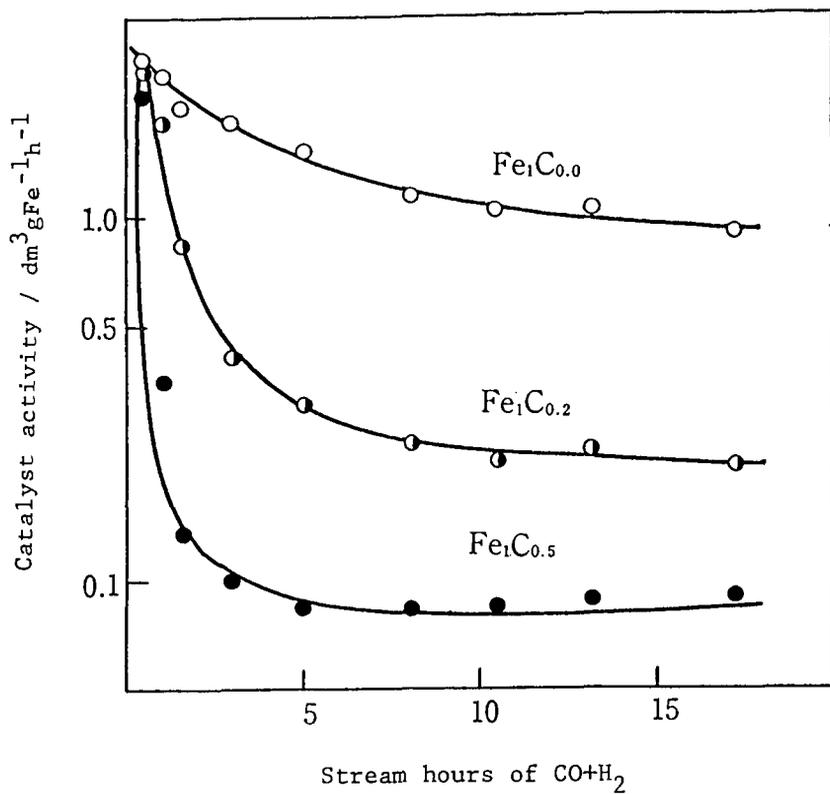


Figure 3 Catalyst Activity vs. Stream Hours of Synthesis Gas in the Fixed-bed Process

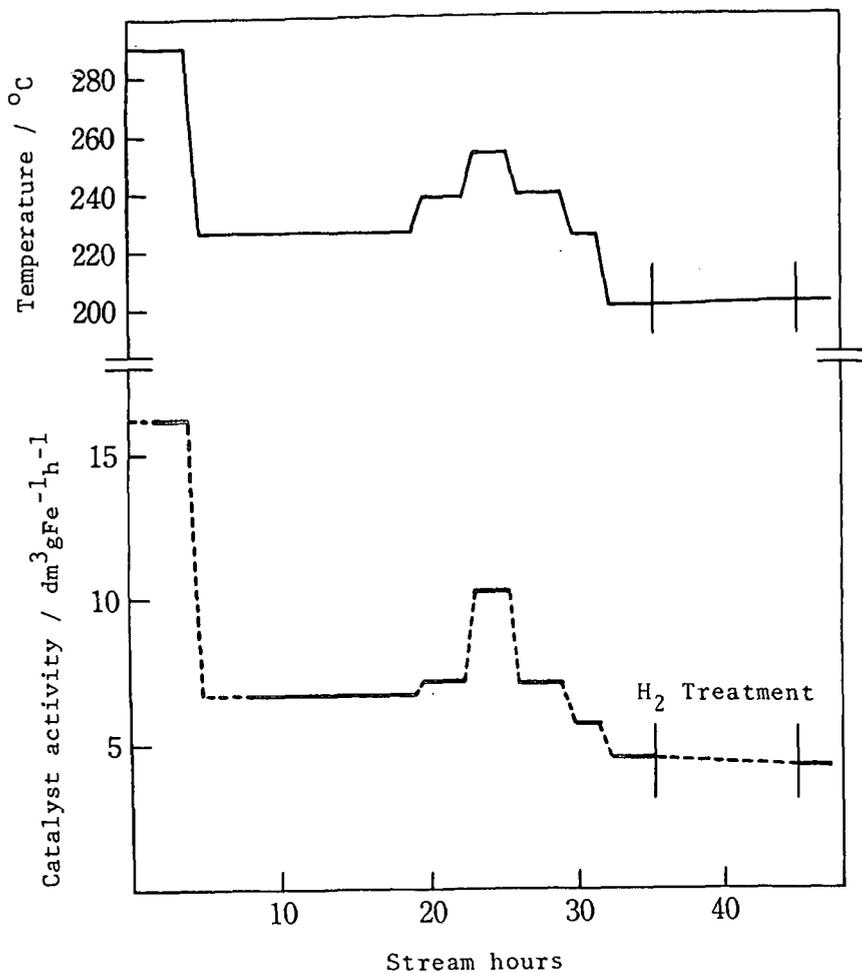


Figure 4 Catalyst Activity vs. Stream Hours of Synthesis Gas in the Oil-slurry Process