The Development of Precipitated Iron
Catalysts with Improved Stability

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Contract Objective

The objective of this program is to identify the chemical principles governing the deactivation of precipitated iron catalysts during Fischer-Tropsch synthesis and to use these chemical principles in the design of catalysts suitable for slurry reactors. The performance targets are 88% CO+H₂ conversion with less than 1% deactivation/day for 1 month and a methane and ethane selectivity of no more than 7% (based on hydrocarbons and oxygenates only) at a space velocity of at least 2 normal liters per hr per gram iron (NL/hr/gFe) using a synthesis gas with 0.5-1.0 H₂:CO ratio in a slurry reactor.

Contract Tasks

- Task 1.0: Develop an integrated pilot plant
- Task 2.0: Evaluate a reference iron catalyst
- Task 3.0: Develop a baseline iron catalyst
- Task 4.0: Elucidate the deactivation chemistry for iron catalysts
- Task 5.0: Investigate catalyst chemistry approaches for improved stability
- Task 6.0: Write final report

Scope of the Work

Previous work under this contract involved the following:

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9/16/87-3/16/88

Task 3.0: four catalysts were prepared by precipitation at different pH levels and were characterized.

3/16/88-6/16/88

Task 1.0: the design work necessary for upgrading the existing fixed-bed pilot plant with slurry and Berty reactor testing capabilities was completed.

6/16/88-9/16/88

Task 3.0: a catalyst preparation plant was designed and constructed.

9/16/88-12/16/88

Task 2.0: experiments determined that the fused iron ammonia synthesis catalyst C-73-1-101 cannot be properly activated in situ in the fixed-bed pilot plant at the relatively low temperatures of 200-300°C, that are typical of the Fischer-Tropsch process.

Task 3.0: an experimental iron catalyst tested in the fixed-bed pilot plant was shown to have acceptable stability and higher than desired methane and ethane selectivity.

12/16/88-3/16/89

Task 2.0: the MCSG-4 catalyst from Mobil was shown to have unexpectedly low activity in the fixed-bed reactor test.

3/16/89-6/16/89

Task 3.0: the construction of the slurry autoclave pilot plant was completed, and an experimental iron catalyst was used for plant shakedown.

6/16/89-9/16/89

Task 3.0: the filter assembly in the autoclave reactor was modified, and an experimental iron catalyst was tested with the new configuration. The ceramic filter with 0.15 μ m pore size plugged during the test.

9/16/89-3/31/90

Task 3.0: filters with larger pore sizes were used to withdraw liquid from the autoclave reactor. The filter with a pore size of $0.7\ \mu\text{m}$ plugged during the test. Filters with a pore size of 5 and $17\ \mu\text{m}$ did not plug but allowed substantial amount of catalyst to pass through.

In this reporting period, several different filtration procedures were evaluated.

Experimental

The slurry-bed pilot plant was previously described in the technical progress report covering the period of 3/16/88 to 6/16/88. The filter assembly, the stirring procedure, and the feed system were described in the technical progress report covering the period of 6/16/89 to 9/16/89. Nine runs were conducted during this reporting period (Runs 10 to 18). The iron catalyst identifications, the nature of initial wax medium, the catalyst and initial wax weights, the heights of the static slurry, and the locations and the pore sizes of the filters are summarized in Table 1. The catalyst and the C_{32} paraffin initial wax medium were loaded to the 1-L autoclave reactor at 120°C . The 4-L autoclave was not used for this work. The 1-L autoclave was pressure-tested with N_2 at 120°C and 18 atm. After a successful pressure test, the pressure was lowered to 11 atm, and the temperature was increased to 280°C under N_2 flow. Synthesis gas with $\text{H}_2:\text{CO}$ feed ratio of 0.7:1 was introduced at 280°C . During the first 12 hr (except for Run 10, which was 6 hr), the catalyst was activated at 280°C and 11 atm using a space velocity of 1.9 to 2.0 NL/hr/gFe. Conditions were changed between 12 and 18 hr on-stream. The temperature was set at 258°C , the pressure at 15 atm, and the space velocity at 1.3-1.4 NL/hr/gFe. Autoclave internal temperatures, pressures, feed compositions, feed rates, space velocities, and stirrer speeds in revolutions per minute (rpm) at different hr on-stream are also summarized in Table 1.

Argon was present in the synthesis gas feed at about 6% (by mole) level and was used as an internal standard for determining conversions and light hydrocarbon selectivities according to the following expressions:

$$\text{CO Conversion, \%} = (((\text{CO/Ar})_{\text{feed}} - (\text{CO/Ar})_{\text{product}}) / (\text{CO/Ar})_{\text{feed}}) * 100$$

The calculation for carbon atom selectivity to CO_2 was:

$$((\text{CO}_2/\text{Ar})_{\text{product}} / ((\text{CO/Ar})_{\text{feed}} - (\text{CO/Ar})_{\text{product}})) * 100$$

The carbon atom selectivity to a hydrocarbon with n carbons, C_n , was:

$$((\text{C}_n/\text{Ar})_{\text{product}} * n / ((\text{CO/Ar})_{\text{feed}} - (\text{CO/Ar})_{\text{product}})) * (100 / (100 - \text{CO}_2 \text{ Selectivity})) * 100$$

The hydrocarbon and oxygenate carbon atom selectivities were normalized to a total of 100% to back out the CO that was converted to CO_2 .

Results and Discussion

In previous tests, both the liquid product and the effluent gas exited the autoclave reactor through the filter. With Run 10, the autoclave was modified so that the effluent gas passed through an independent outlet port situated at the top of the autoclave. The autoclave pressure was controlled by a back-pressure regulator in the effluent gas line. The pressure drop across the filter used for draining the liquid products was controlled by independently regulating the pressure at the exit of the filter. This new filtration configuration was maintained for the rest of the work as well.

In Run 10, the metallic filter had a nominal pore diameter of 1 μm and an absolute pore diameter of 5 μm and was totally immersed in the liquid. A block valve past the filter was opened once a day, and about 0.7 atm pressure drop was exerted in an attempt to drain some of the liquid out of the autoclave. Substantial amounts of catalyst loss occurred during this procedure. Also, the filter plugged.

To prevent the catalyst loss problem, a $0.7\text{ }\mu\text{m}$ ceramic filter was used in Run 11. The filter was back-flushed with the synthesis gas that passed through the filter. No draining was done during the first 28 hr and the liquid level in the autoclave increased by about 3 in. At 28 hr on-stream, the feed was diverted from the filter to the dip-leg, and about 0.2 atm pressure drop was exerted. This drop in pressure caused about 2 in. of liquid to drain out (Figure 1). No further draining was done in Run 11, and therefore, the liquid level continued to rise during the later part of the test. A similar draining procedure was also successfully used in Run 12. However, in both Runs 11 and 12, significant problems were encountered in sealing the ceramic filter against the stainless steel tube extending from the autoclave head.

Operational problems occurred in Runs 13 and 14, and therefore, these runs were terminated early. Runs 15 to 18 used a metallic filter to overcome the sealing problems observed with ceramic filters. The filter nominal pore size was $0.5\text{ }\mu\text{m}$. The filter was immersed in liquid, as was the case in Runs 10 to 12. However, when the draining procedure that was used in Runs 10 to 12 with the ceramic filter was applied to the metallic filter in Runs 15 to 17, draining was extremely fast, causing most of the liquid inventory of the autoclave to be lost (Figure 2).

To prevent the loss of the liquid inventory, the filter level was raised to 5-5/8 in. from the bottom of the autoclave in Run 18, so that the bottom of the filter ($0.5\text{ }\mu\text{m}$) was 1-1/16 in. above the initial static slurry level. The slurry level gradually increased during the first 40 hr, after which the filter acted as a liquid level controller (Figure 3). Two filters were used. One of the filters was being continuously back-flushed with nitrogen gas, and the other one was used for draining the liquid. At the end of a 4-hr cycle, the filters were switched. Draining of the liquid products typically required about 1 atm pressure drop. The liquid level was successfully maintained between 6 and 6.5 in. until 100 hr on-stream. Both filters plugged after 100 hr, and the run was terminated at the end of 126 hr.

In Run 18, a down-flow propeller was placed on the stirring shaft 1-1/4 in. above the impeller in order to achieve good mixing. During the run, the CO conversion decreased from 80% to 60%, and the methane selectivity increased from 1.5% to 4.2% (see Figures 5 and 6).

Summary

The slurry autoclave was modified so that the pressure drop across the filter can be controlled independently from the autoclave pressure. Draining of the liquid product out of the autoclave was achieved typically with a pressure drop of no more than 1 atm. Difficulties were encountered in sealing the ceramic filters against stainless steel tubes in the autoclave reactor. At comparable pore size, draining appeared to be much faster with a metallic filter. A 0.5- μ m metallic filter maintained the liquid level successfully for about 100 hr in the autoclave reactor. The liquid was maintained at a level that corresponds approximately to the bottom of the filter.

An experimental iron catalyst showed a gradual decline in CO conversion from 80% to about 60% during the 126-hr test in Run 18. Longer testing periods are necessary to evaluate catalytic stability. These tests will be carried out during the next quarter. During the same run, the selectivity to methane first showed a gradual increase and then lined out at about 4.2%. Because the selectivity to ethane is about 1%, the overall methane and ethane selectivity seems to be within target.

Table 1
Run Information

Run	Plant	Catalyst					Wax Medium				Temp in, °C	Filter		Press Out, atm	Feed						Hr
		Number	Fe, %		Wt., g	Mesh Size	Static Ht. in.	Nature	Solids, %	Wt., g (wax)	Rpm	Pore Size, µm	Height in.		H ₂ , %	CO, %	Ar, %	H ₂ CO	Rate sec/min	NL/h /gFe	
9	700B	5709- 139	64		95	140-400	4-5/8	C ₃₂	20	380	1000	5-18	4-14/16	11	39.49	54.77	5.74	0.72	1980	1.9	0-12
											↓			↓	39.49	54.62	5.89	0.72	1420	1.4	12-14
											1100			15	↓	↓	↓	↓			14-28
											1200			↓	↓	↓	↓	↓			28-30
											1300	↓		↓	39.35	54.95	5.88	↓	↓	↓	30-78
10	700B	5709- 184	67.4		95	140-400	4-5/8	C ₃₂	20	380	1300	1-5	2-3/4	11	39.31	54.13	6.63	0.72	1980	1.9	0-6
											↓			15	↓	↓	↓	↓	1420	1.3	6-24
											↓			↓	↓	↓	↓	↓	↓	↓	24-36
11	700B	5709- 184	67.4		95	140-400	4-9/16	C ₃₂	20	380	1300	0.7	2-7/8	11	36.76	56.44	6.32	0.65	1980	1.9	0-12
											↓			↓	↓	↓	↓	↓	1420	1.30	12-14
											↓			15	39.48	53.98	6.60	0.73	↓	↓	14-18
											↓			↓	↓	↓	↓	↓	1080	1.0	18-38
											↓			↓	39.29	54.16	6.53	0.73	710	0.67	38-84

Table 1

R'n	Plant	Catalyst					Wax Medium					Temp in, °C	Filter		Press Out, atm	Feed					Hr
		Number	Fe, %		Wt., g	Mesh Size	Static Ht, in.	Nature	Solids, %	Wt., g (wax)	Rpm		Pore Size, μm	Height in.		H ₂ , %	CO, %	Ar, %	H ₂ -CO	Rate sec/min	
12	700B	5709-184	67.4		95	140-400	4-9/16	C ₃₂	20	380	1300	0.7	2-7/8	11	39.29	54.16	6.55	0.73	1982	1.9	0-12
											↓			11 ↑ 15	40.18	53.29	6.53	0.75	1415	1.3	12-18
											↓			15					1415 486	1.3 0.46	18-28
															↓			↓	486	0.46	28-76
															40.5	52.99	6.51	0.76			76-131
															40.41	53.51	6.08	0.76			131-154
13	700B	5709-184	67.4		95	140-400	4-9/16	C ₃₂	20	380	1300	0.15	2-7/8	11				0.7	1980	1.9	0-12
											↓			11 ↑ 15					1420	1.3	12-18
											↓			15				↓			18
14	700B	5709-184	67.4		95	140-400	4-9/16	C ₃₂	20	380	1300	0.15	2-7/8	11				0.7	1980	1.9	0-12
											↓			11 ↑ 15				↓	1420	1.3	12-18
											↓			15				↓			18-

Table 1

[illegible]

Table 1

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FIGURE 1
LIQUID LEVEL Vs. HOURS ON-STREAM
FOR RUN 11 IN PLANT 700B

FIGURE 2
LIQUID LEVEL Vs. HOURS ON-STREAM
FOR RUN 16 IN PLANT 700B

FIGURE 3
LIQUID LEVEL Vs. HOURS ON-STREAM

FOR RUN 18 IN PLANT 700B

FIGURE 4

EVALUATION OF PRECIPITATED IRON CATALYST 5709-184 IN SLURRY REACTOR 700B DURING RUN 18

FIGURE 5

EVALUATION OF PRECIPITATED IRON CATALYST 5709-184 IN SLURRY REACTOR 700B DURING RUN 18

**DATE
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7/20/92