9. Conclusions

While many objectives of the experimental program have been satisfied, a number of conditions have been observed which raise additional questions with regard to rates of carbon formation during methanation. It is readily apparent from the experimental results that thermodynamic equilibrium data are of little use in predicting carbon formation, the type of carbon and the rate at which it forms. It is equally apparent that, for a given feed gas/catalyst combination operating at conditions which have been previously shown to result in carbon formation, there are circumstances which can completely alter the experimental behavior, such that carbon will not be formed, e.g., treatment with 100 percent steam. Unfortunately, these circumstances are not yet well understood.

TABLE IV-D-3

Physical & Compositional Data of Catalysts Used

	G-87P	G-87P(T)	Ni-104T
Manufacturer	United Catalyst	United Catalyst	Harshaw
Size	1/8" extrudate	3/16" x 1/8" tablet	1/8" tablet
Surface Area, M^2/gm	56 (oxide)	34 (reduced) (1)	150 (reduced)(1)
Pore Volume, $^{cc}/gm$	0.42 (oxide)	0.2 (reduced)(1)	0.25 (reduced)(
	0.41 (reduced)		
Ni, wt%	38	38	58
Ni Crystallite Size, Å	106 (oxide)(2)	219 (reduced)(3)	64 (reduced)(3)
	120 (reduced)(3)		
Carrier	Alumina/Co Promoted	Alumina/Co Promoted	Kieselguhr
Carbon, wt%	2.0 (oxide)	2.0 (oxide)	3.0 (reduced)
	0.5 (reduced)	0.5 (reduced)	

(1) Stabilized with CO absorption

(2) NiO crystal size

(3) NiO also present

Table IV-D-4: Analytical Results of Spent Catalysts

Run	Catalyst	Operating Conditions	Carbon (wt.%)	Surface Area (m^2/gm)	Pore Volume (cc/gm)	X-Ray Diffraction Data (Å) Ni	α-Al_2O_3	$CaCO_3$	Graphite	Others
1	G-87P	35 atm, 480°C, 0% stm, 500 hrs	9.2	46	0.61	203	2000	2000	300	γ-Al_2O_3
			4.8	—	—	—	—	—	—	—
			4.5	—	—	—	—	—	—	—
			4.5	—	—	—	—	—	—	—
2	G-87P	35 atm, 480°C, 5% stm, 500 hrs	7.4	44	0.49	203	2000	2000	300	γ-Al_2O_3
			5.2	—	—	—	—	—	—	—
			5.2	—	—	—	—	—	—	—
			4.9	—	—	—	—	—	—	—
3	G-87P	35 atm, 480°C, 30% stm, 500 hrs	6.3	42	0.52	357	2000	1400	300	γ-Al_2O_3
			5.2	—	—	—	—	—	—	—
			5.5	—	—	—	—	—	—	—
			5.8	46	—	—	—	—	—	—
4	G-87P	35 atm, 315°C, 0% stm, 500 hrs	3.7	42	0.56	400	>2000	1400	450	γ-Al_2O_3 (1)
			3.4	—	—	—	—	—	—	—
			2.9	—	—	—	—	—	—	—
			2.3	—	—	—	—	—	—	—
5	G-87P	35 atm, 315°C, 5% stm, 300 hrs	4.7	51	0.52	350 (2)	>2000	1450	600	γ-Al_2O_3
			2.9	—	—	—	—	—	—	—
			3.5	—	—	—	—	—	—	—
			3.5	—	—	—	—	—	—	—
5a	G-87P	35 atm, 315°C, 5% stm, 220 hrs	—	—	—	—	—	—	—	—
5b	G-87P	35 atm, 315°C, 5% stm, 500 hrs	4.8	—	—	—	—	—	—	—
			4.6	—	—	—	—	—	—	—
			4.3	—	—	—	—	—	—	—
			4.5	61	—	357	2000	1405	360	—

Table IV-D-4 (continued)

Run	Catalyst	Operating Conditions	Carbon (wt.%)	Surface Area (m^2/gm)	Pore Volume (cc/gm)	X-Ray Diffraction Data (Å) Ni	α-Al_2O_3	$CaCO_3$	Graphite	Others
6	G-87P	69 atm, 480°C, 0% stm, 500 hrs	3.7	44	0.53	198	>2000	>2000	275	γ-Al_2O_3
			2.8	—	—	—	—	—	—	—
			4.0	—	—	—	—	—	—	—
			3.5	—	—	—	—	—	—	—
7	G-87P	69 atm, 480°C, 5% stm, 500 hrs	5.1	10.6	0.48	350	~2000 (3)	>2000	300	γ-Al_2O_3 (1)
			4.2	—	—	—	—	—	—	—
			4.3	—	—	—	—	—	—	—
			3.6	39	—	—	—	—	—	—
8	G-87P	35 atm, 480°C, 3.85% stm, 100 hrs	0.8	35	0.52	258	>2000	488	—	γ-Al_2O_3
			0.8	—	—	—	—	—	—	—
			0.9	—	—	—	—	—	—	—
			0.7	—	—	—	—	—	—	—
8a	G-87P	35 atm, 480°C, 3.85% stm, 0 hrs	0.5	44	0.41	120 (4)	>2000	Trace	—	—
			—	—	—	—	—	—	—	—
			—	—	—	—	—	—	—	—
			—	—	—	—	—	—	—	—
8b	G-87P	35 atm, 480°C, 3.85% stm, 25 hrs	0.7	—	—	—	—	—	—	—
			0.8	—	—	—	—	—	—	—
			0.7	—	—	—	—	—	—	—
			0.6	—	—	—	—	—	—	—
8c	G-87P	35 atm, 480°C, 3.85% stm, 50 hrs	0.8	—	—	—	—	—	—	—
			0.8	—	—	—	—	—	—	—
			0.8	—	—	—	—	—	—	—
			0.7	—	—	—	—	—	—	—
8d	G-87P	35 atm, 480°C, 3.85% stm, 100 hrs	0.6	—	—	—	—	—	—	—
			0.7	—	—	—	—	—	—	—
			0.7	—	—	—	—	—	—	—
			0.7	—	—	—	—	—	—	—
9	G-87P	35 atm, 480°C, 3.85% stm, 310 hrs	5.3	44	0.48	172	>2000	736	210	γ-Al_2O_3
			5.2	—	—	—	—	—	—	—
			4.5	—	—	—	—	—	—	—
			5.2	—	—	—	—	—	—	—

Table IV-D-4 (continued)

Run	Catalyst	Operating Conditions	Carbon (wt.%)	Surface Area (m^2/gm)	Pore Volume (cc/gm)	X-Ray Diffraction Data (Å) Ni	α-Al_2O_3	$CaCO_3$	Graphite	Others
10	G-87P	35 atm, 480°C, 3.85% stm, 600 hrs	3.4	32	0.53	379	~2000	>2000	—	γ-Al_2O_3
			1.7	—	—	—	—	—	—	—
			1.1	—	—	—	—	—	—	—
			0.9	—	—	—	—	—	—	—
11	G-87P	35 atm, 480°C, 3.85% stm, 910 hrs	9.7	35	0.50	299	~2000	>2000	300	γ-Al_2O_3
			3.4	—	—	—	—	—	—	—
			1.6	—	—	—	—	—	—	—
			3.7	—	—	—	—	—	—	—
12	G-87P	35 atm, 480°C, 3.85% stm, 1200 hrs	1.4	29	0.54	393(5)	>2000	485	—	γ-Al_2O_3(6)
			1.8	—	—	—	—	—	—	—
			0.9	—	—	—	—	—	—	—
			1.0	—	—	—	—	—	—	—
12a	G-87P	35 atm, 480°C, 3.85% stm, 1105 hrs	2.2	—	—	—	—	—	—	—
			1.5	—	—	—	—	—	—	—
			1.2	—	—	—	—	—	—	—
			1.0	—	—	—	—	—	—	—
13	Used G-87P	35 atm, 480°C, 5% stm, 500 hrs	8.5	43	0.45	210	~2000	>2000	370	γ-Al_2O_3
			3.8	—	—	—	—	—	—	—
			2.9	—	—	—	—	—	—	—
			3.1	—	—	—	—	—	—	—
14	Ni-104T	35 atm, 480°C, 30% stm, 500 hrs	3.3	76	0.21	101	—	—	1070	—
			3.2	—	—	—	—	—	—	—
			3.0	—	—	—	—	—	—	—
			3.1	—	—	—	—	—	—	—
15	Ni-104T	35 atm, 480°C, 0% stm, 500 hrs	3.4	77	0.16	101(7)	Trace	—	1807	—
			3.4	—	—	—	—	—	—	—
			2.9	—	—	—	—	—	—	—
			3.1	—	—	—	—	—	—	—
16	Ni-104T	35 atm, 480°C, 5% stm, 500 hrs	3.1	83	0.27	88(7)	—	—	1807	—
			3.2	—	—	—	—	—	—	—
			2.9	—	—	—	—	—	—	—
			3.0	—	—	—	—	—	—	—

Table IV-D-4 (continued)

Run	Catalyst	Operating Conditions	Carbon (wt.%)	Surface Area (m^2/gm)	Pore Volume (^{cc}/gm)	X-Ray Diffraction Data (Å) Ni	α-Al_2O_3	$CaCo_3$	Graphite	Others
17	Ni-104T	35 atm, 480°C, 3.85% stm, 96 hrs	3.1	97	0.20	81 (7)	—	—	>2000	—
			3.0	—	—	—	—	—	—	—
			3.1	—	—	—	—	—	—	—
			3.1	—	—	—	—	—	—	—
18	Ni-104T	35 atm, 480°C, 3.85% stm, 280 hrs	2.5 (8)	86	0.16	>2000	>2000	—	1807	—
			3.0	—	—	—	—	—	—	—
18a	Ni-104T	35 atm, 480°C, 3.85% stm, 307 hrs	3.6	77	0.18	101	Trace	—	1807	—
			3.3	—	—	—	—	—	—	—
			3.2	—	—	—	—	—	—	—
			3.2	—	—	—	—	—	—	—
19	Ni-104T	35 atm, 480°C, 3.85% stm, 570 hrs	3.4	75	0.17	103	Trace	—	1807	—
			3.0	—	—	—	—	—	—	—
			3.1	—	—	—	—	—	—	—
			3.3	—	—	—	—	—	—	—
20	Ni-104T	35 atm, 480°C, 3.85% stm, 1200 hrs	3.6	79	0.19	101	Trace	—	1912	—
			3.3	—	—	—	—	—	—	—
			3.2	—	—	—	—	—	—	—
			3.2	—	—	—	—	—	—	—
21	Ni-104T	35 atm, 480°C, 3.85% stm, 620 hrs	3.3	68	0.19	101 (9)	Trace	Trace	981	—
			3.2	—	—	—	—	—	—	—
			3.3	—	—	—	—	—	—	—
			3.1	—	—	—	—	—	—	—
22	Ni-104T	35 atm, 315°C, 0% stm, 500 hrs	4.4	—	—	—	—	—	—	—
			4.6	—	—	—	—	—	—	—
			3.7	—	—	—	—	—	—	—
			3.5	56	0.19	105	Trace	Trace	1807	—
23	Ni-104T	35 atm, 315°C, 5% stm, 500 hrs	4.1	—	—	—	—	—	—	—
			3.7	—	—	129	Trace	Trace	1807	—
			3.5	—	—	—	—	—	—	—
			3.6	85	0.18	91	Trace	Trace	1807	—

Table IV-D-4 (continued)

Run	Catalyst	Operating Conditions	Carbon (wt.%)	Surface Area (m^2/gm)	Pore Volume (cc/gm)	X-Ray Diffraction Data (Å) Ni	α-Al_2O_3	$CaCO_3$	Graphite	Others
24	G-87P(T)	35 atm, 480°C, 0% stm, 505 hrs	0.7	49	0.31	158 (15)	>2000	1300	—	γ-Al_2O_3
			0.8	—	—	—	—	—	—	—
			0.9	—	—	—	—	—	—	—
			0.9	—	—	—	—	—	—	—
25	G-87P(T)	35 atm, 480°C, 5% stm, 505 hrs	0.8	45	0.32	192	>2000	1475	—	—
			0.9	—	—	—	—	—	—	—
			0.9	—	—	—	—	—	—	—
			1.1	—	—	—	—	—	—	—
	G-87P	oxide form	2.0	56	0.42	106 (10)	>2000	414	300	Co_3O_4 (11)
	G-87P	reduced & stabilized	0.5	44	0.41	179 (12)	>2000	>2000	—	—
	G-87P(T)	reduced & stabilized	0.5	34	0.20	219 (13)	>2000	1074	308	—
	Ni-104T	reduced & stabilized	3.0	150	0.20	64	—	—	1370 (5)	—

(1) Trace of X $Ni(OH)_2$ - NiOOH

(2) 40% NiO (450 Å)

(3) Also α-$Al_2O_3 \cdot H_2O$ (1800 Å)

(4) NiO @ 200 Å

(5) Trace of NiO

(6) 412 Å

(7) NiO present <60 Å

(8) The used catalyst was analyzed for top half and bottom half only.

(9) Possible NiO

(10) As NiO

(11) ~500 Å

(12) 73% Ni & 27% NiO (160 Å)

(13) 44% Ni & 56% NiO (99 Å)

(14) Reduced only

(15) Presence of NiO

The most important variable in determining the level of carbon formation is the catalyst itself. Under identical operating conditions the G-87P extrudates formed extremely high levels of carbon up to 10 percent, while the Ni-104T formed none, and in fact actually lost some carbon originally present in the tablets. At first one could attribute the different behavior to the fact that the catalysts each use a different carrier, the G-87P uses alpha-alumina, while the Ni-104T uses Kieselguhr. However, the fact is that a tableted version of the G-87P, of exactly the same chemical composition as the extrudate, formed virtually no carbon under the same reaction conditions. Therefore, these differences in behavior arise from much more subtle sources, which involve not only gross physical and chemical properties, but also fine structure details as well.

In addition, it should be noted that in spite of heavy carbon deposition, the catalytic behavior for these systems remains unaffected. The limiting condition would be, it seems, physical plugging of the reactor itself and not catalyst deactivation. In this respect, it may be possible that controlled oxidation of the carbon deposit is a viable method of extending operating life.